



Facoltà di Bioscienze e tecnologie  
agroalimentari e ambientali



# Nanomaterial-based sensing of phenolic compounds and related antioxidant capacity in food

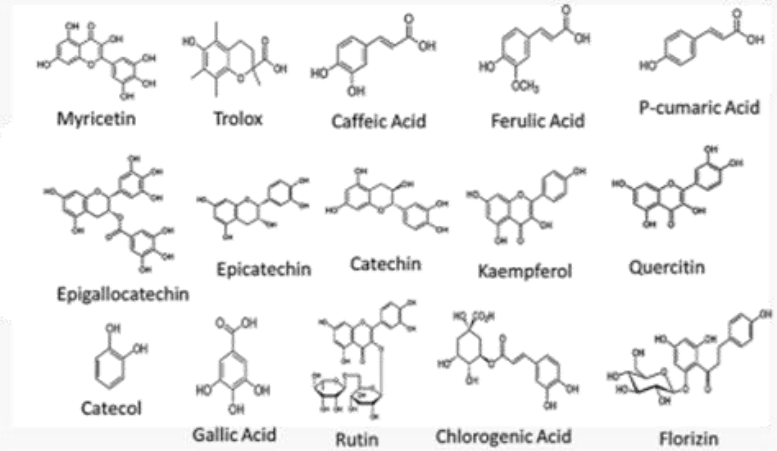
**Dario Compagnone**

Faculty of Biosciences for Food Agriculture and Environment

University of Teramo

# Polyphenol compounds

Heterogeneous class of chemical compounds of considerable interest in the food industry:



Nutritional property / functional food



Sensory characteristics definition  
(bitterness, astringency, etc...)



key role in shelf-life



Indicators of quality



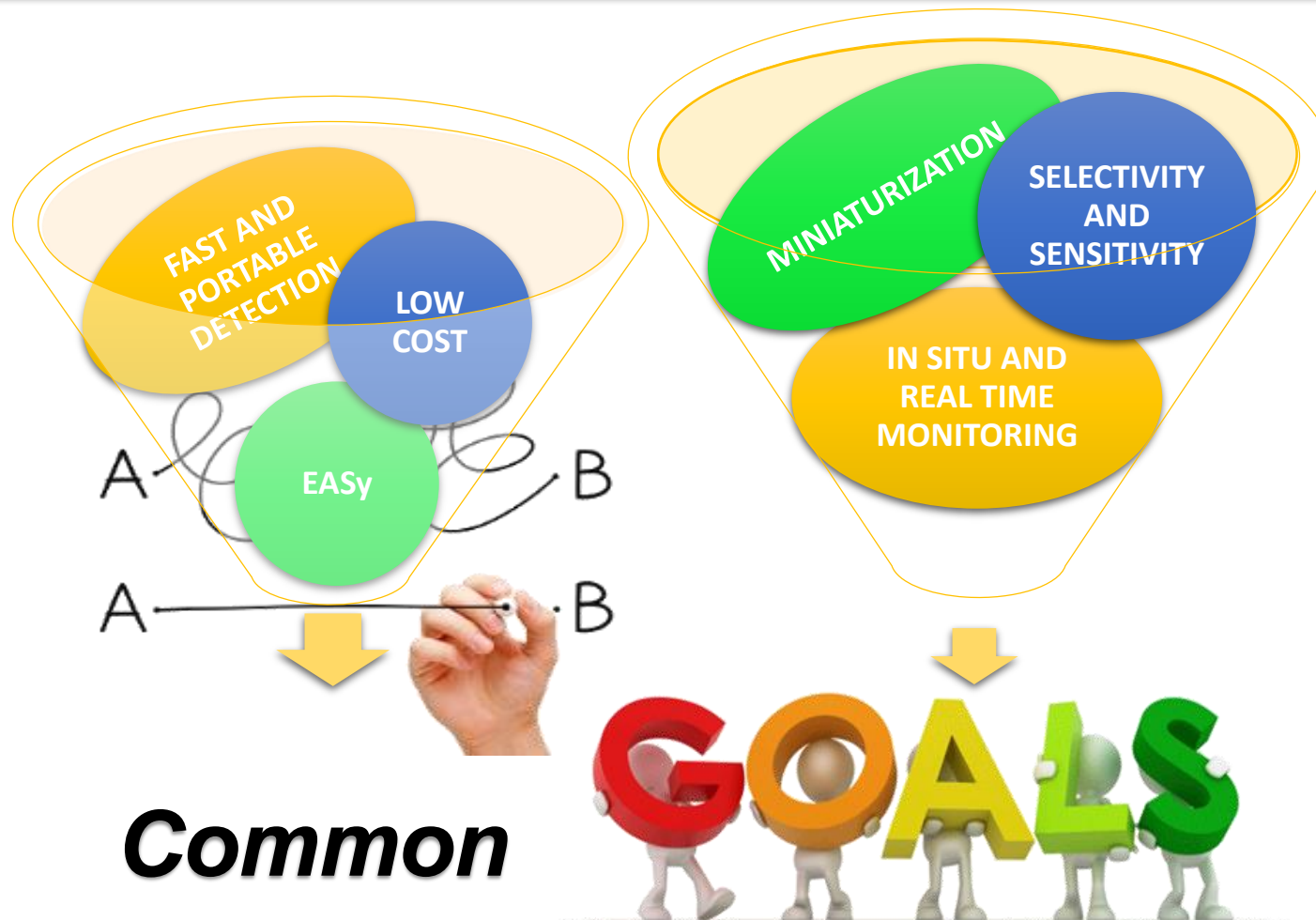
Process indicators



Anti-microbial property

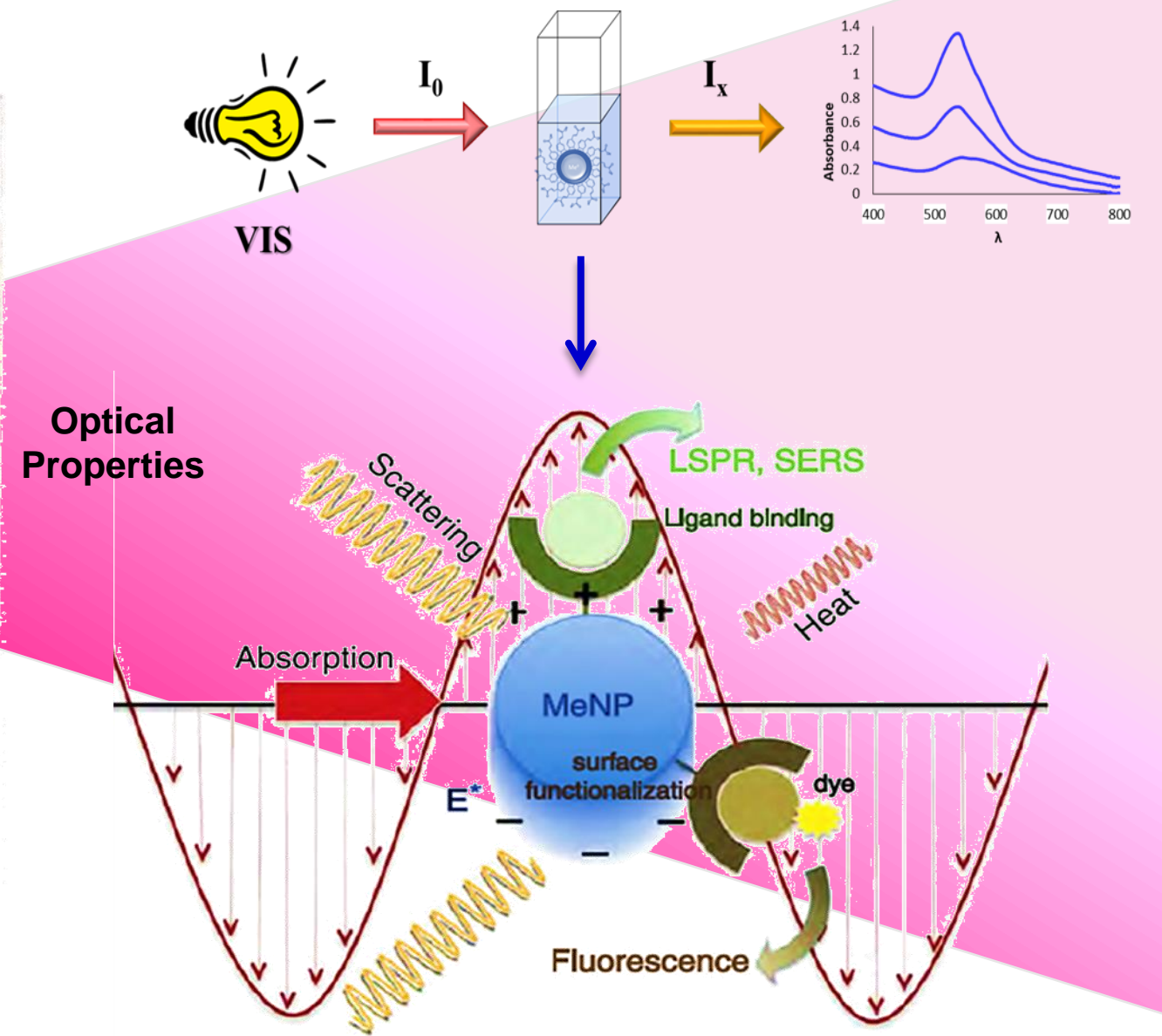
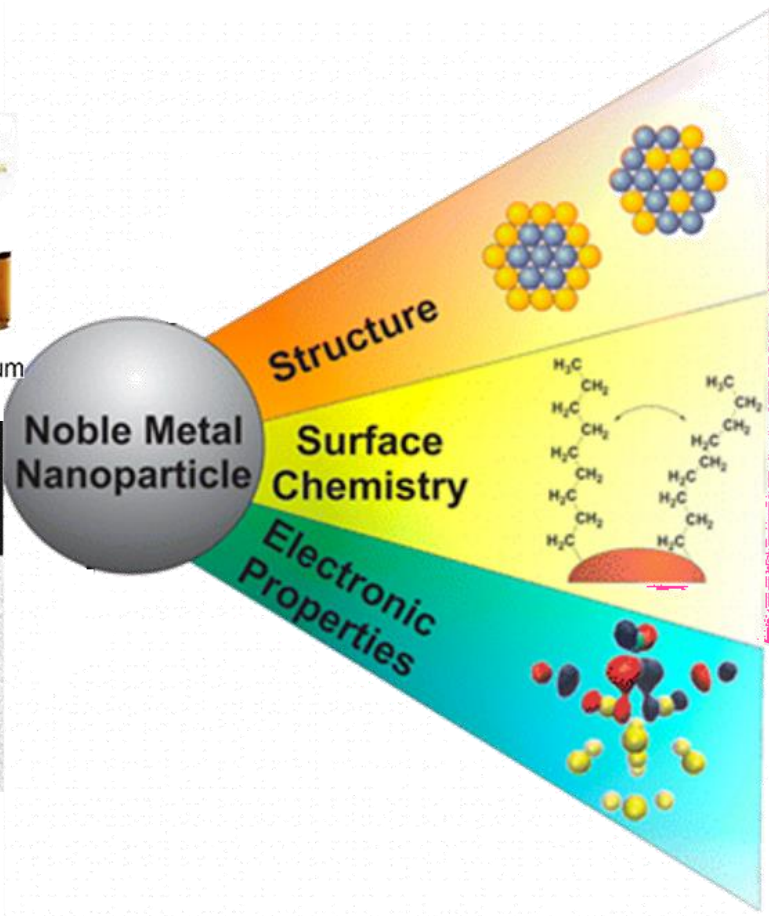
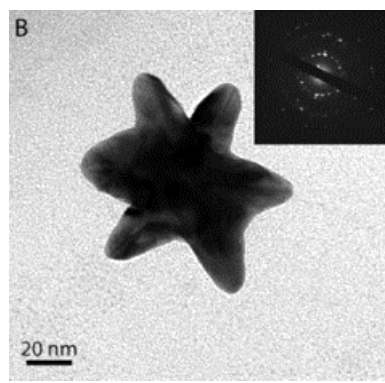
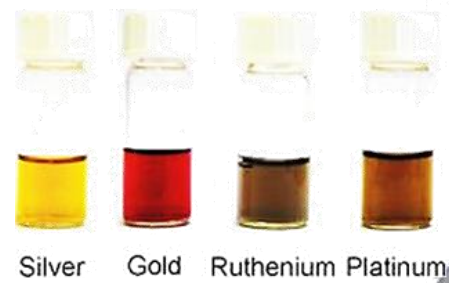
<http://phenol-explorer.eu>

## Nanomaterial-based methodologies for sensing of phenolic compounds and their antioxidant capacity in food



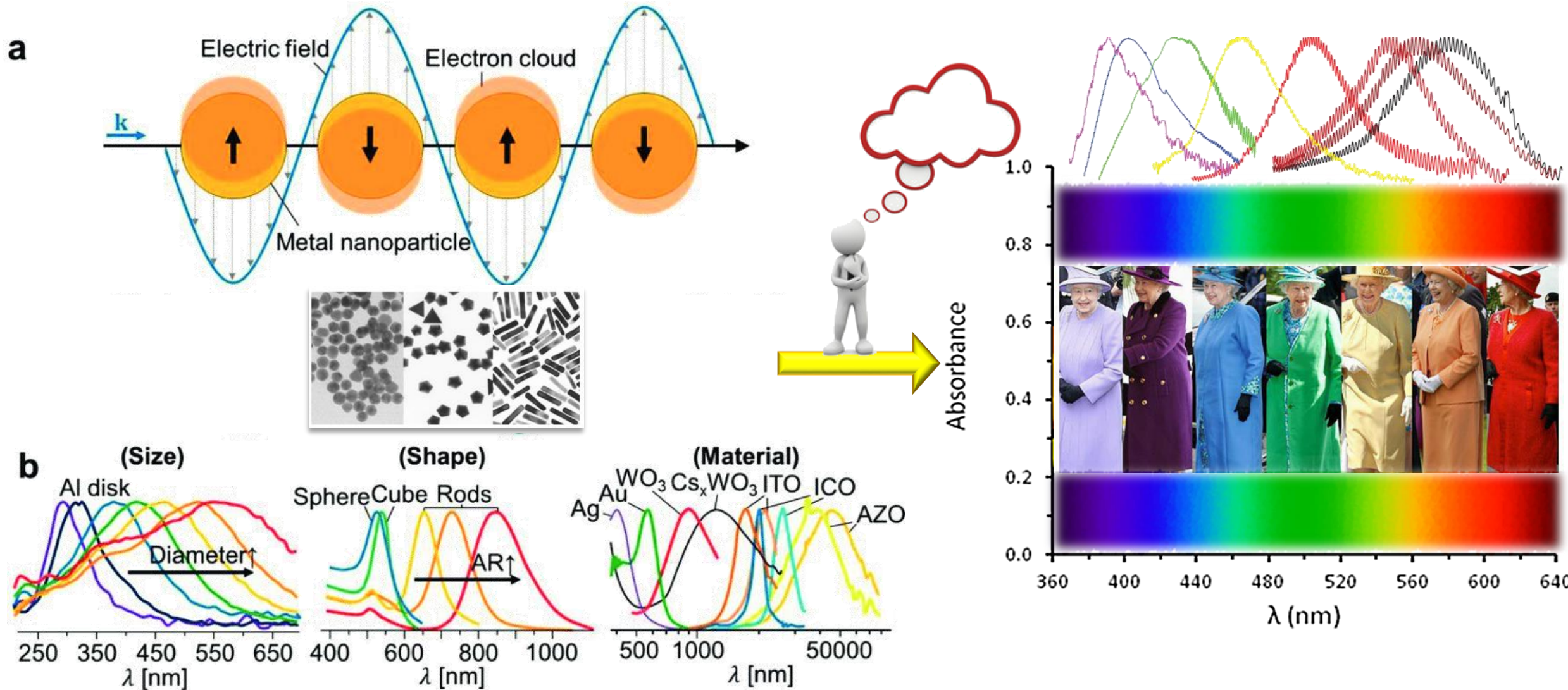
# Metal nanoparticles (MNPs)

## MNPs features



# Metal nanoparticles (MNPs)

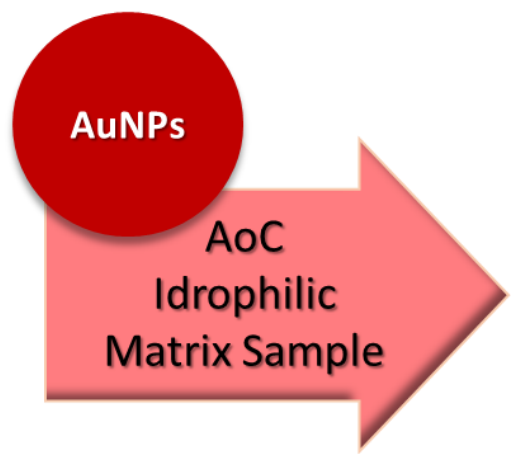
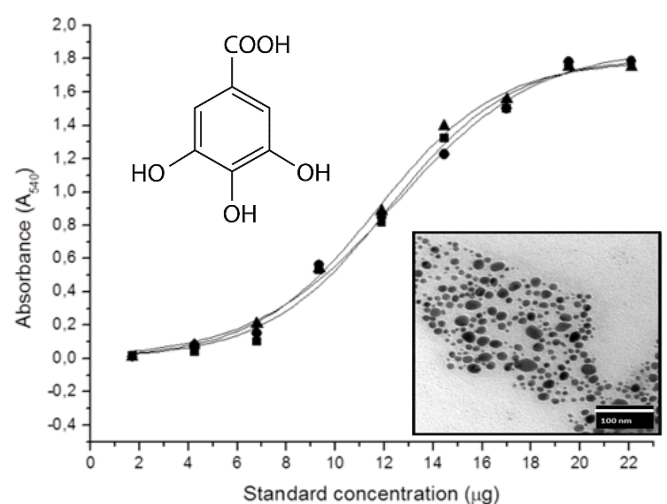
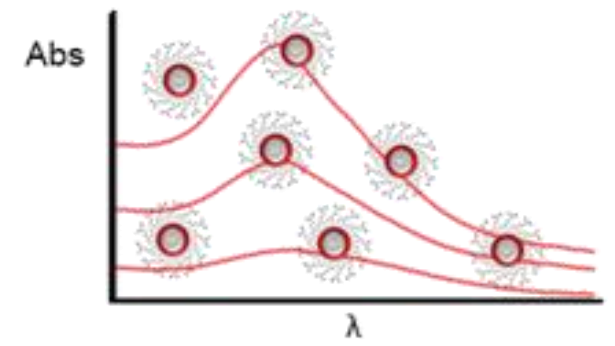
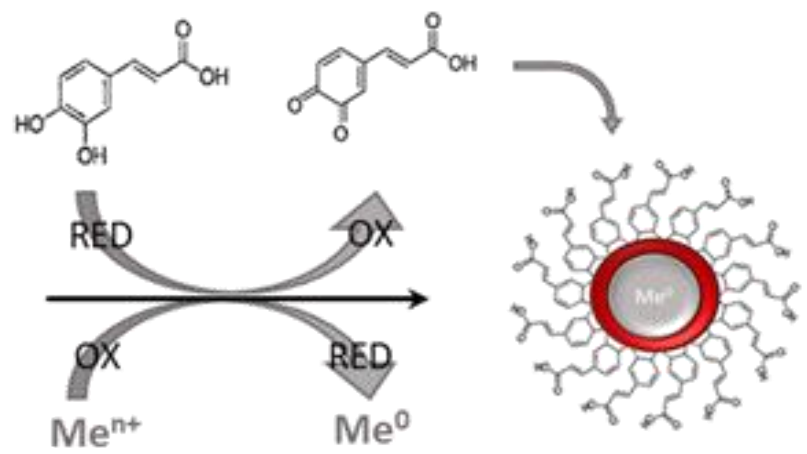
Analytical principle  $\longrightarrow$  Localized Surface Plasmon Resonance (LSPR)



GÉRARD, Davy; GRAY, Stephen K. Aluminium plasmonics. *Journal of Physics D: Applied Physics*, 2014, 48.18: 184001.  
CHEN, Huanjun, et al. Shape- and size-dependent refractive index sensitivity of gold nanoparticles. *Langmuir*, 2008, 24.10: 5233-5237.  
LOUNIS, Sebastien D., et al. Defect chemistry and plasmon physics of colloidal metal oxide nanocrystals. *The journal of physical chemistry letters*, 2014, 5.9: 1564-1574.

# General strategy

*Metal nanoparticles suspensions (MNPs) can be produced by reducing agents*



- **Antioxidant capacity evaluation (AoC):**  
(AuNPs-based AoC index)

- It works on aqueous/hydroalcoholic solutions

*Total assay time: 15-25 min*

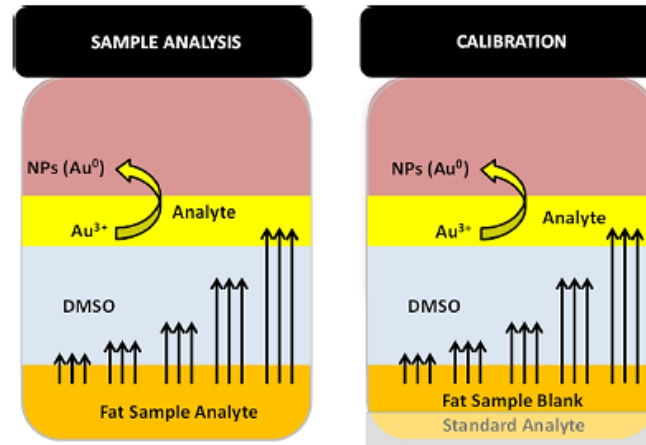
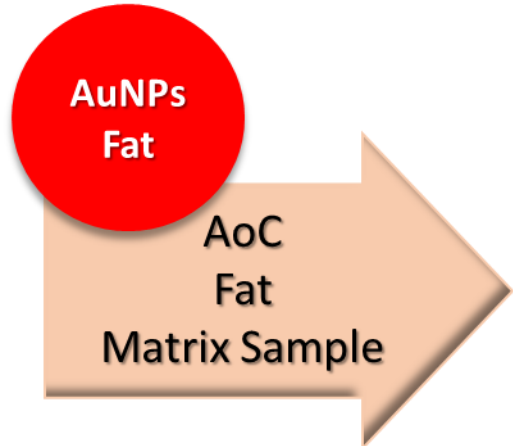
Food Chemistry 178 (2015) 70–75  
 Contents lists available at ScienceDirect  
**Food Chemistry**  
 journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods  
**Antioxidant capacity index based on gold nanoparticles formation. Application to extra virgin olive oil samples**  
 Flavio Della Pelle <sup>a,b</sup>, Diana Vilela <sup>a</sup>, María Cristina González <sup>a</sup>, Claudio Lo Sterzo <sup>b</sup>, Darío Compagnone <sup>b</sup>, Michele Del Carlo <sup>b,\*</sup>, Alberto Escarpa <sup>b,\*</sup>

<sup>a</sup> Departamento de Química Analítica, Química-Física e Ingeniería Química, Facultad de Química, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain  
<sup>b</sup> Facultad de Biociencias e Tecnologías Agro-Alimentarias e Ambientales, Universidad degli Studi di Teramo, 64023 Mosciano Sant'Angelo, Italy

# Metal nanoparticles (MNPs)

## *AuNPS colorimetric assay total polyphenols evaluation directly using lipidic matrices*



- **Total polyphenols determination**
- **Extraction free:** directly applicable in fat sample matrix

*Total assay time: 10 min*

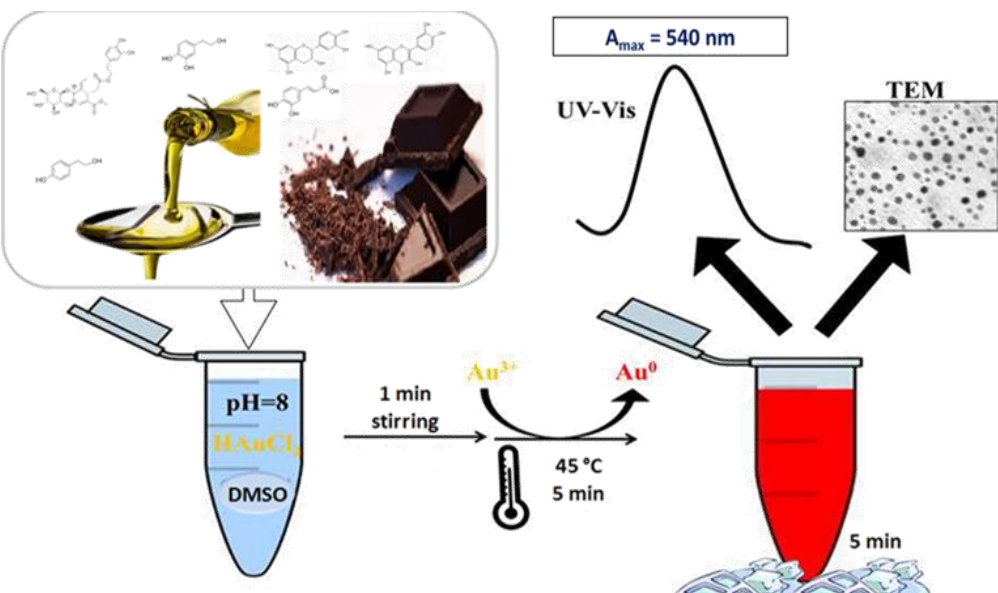
# Metal nanoparticles (MNPs)



AuNPs  
Fat

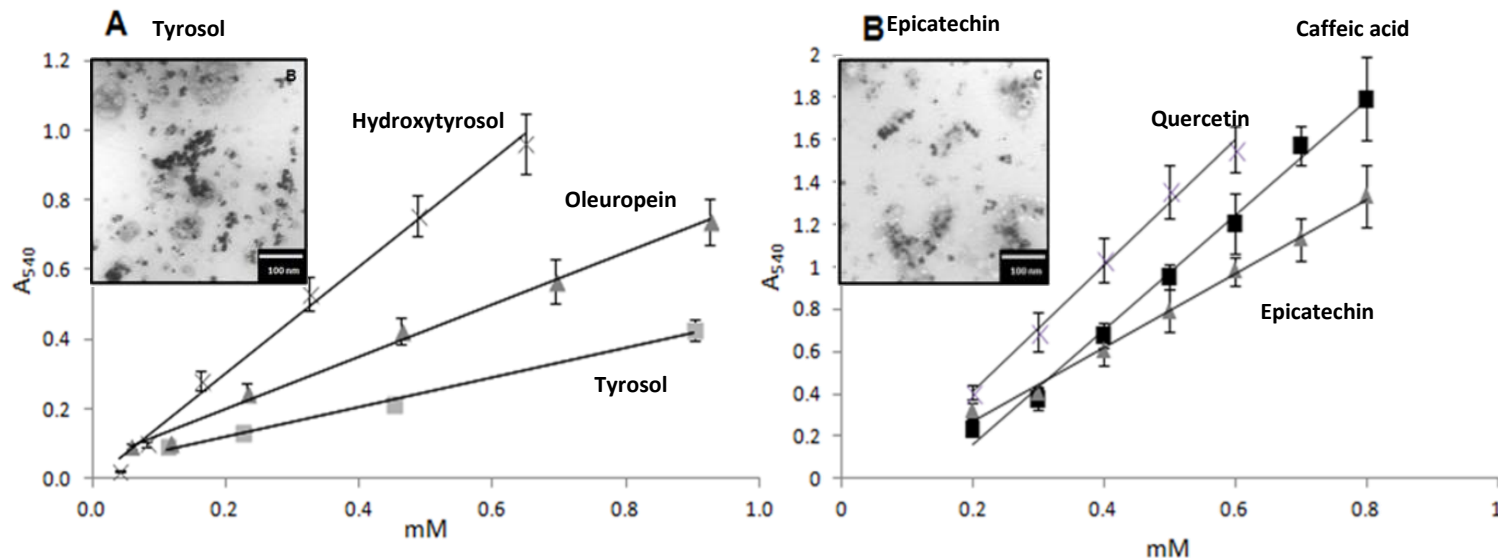
AoC  
Fat  
Matrix Sample

*polyphenolic standards reactivity study :  
(olive oil and chocolate/cocoa polyphenols standards)*



**Olive Oil and chocolate standards are able to form AuNPs**

- LSPRmax ≈ 540nm
- $R^2 \geq 0.992$
- Good reproducibility (RSD ≤ 13, n.=3 inter-day)



(×) Hydroxytyrosol  $R^2 = 0.992$

$$(y = 1.5371x - 0.0054)$$

(▲) Oleuropein  $R^2 = 0.993$

$$(y = 0.7525x + 0.0509)$$

(■) Tyrosol  $R^2 = 0.995$

$$(y = 0.4237x + 0.037)$$

(×) Quercetin  $R^2 = 0.993$

$$(y = 29.59x - 0.1756)$$

(■) Caffeic acid  $R^2 = 0.993$

$$(y = 27.136x - 0.3841)$$

(▲) Epicatechin  $R^2 = 0.994$

$$(y = 17.414x - 0.0753)$$





# Metal nanoparticles (MNPs)

AuNPs  
Fat

AoC

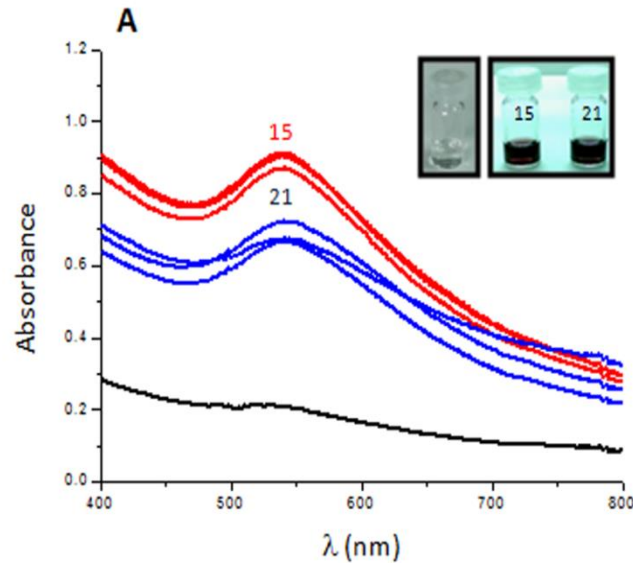
Fat

Matrix Sample

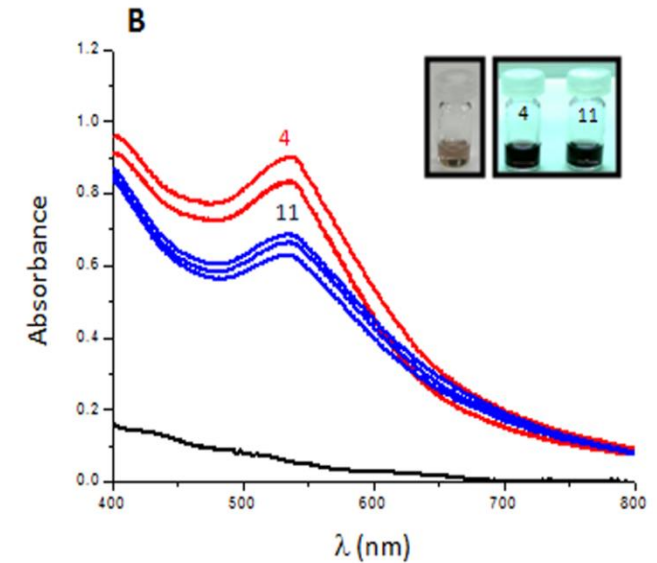
## Samples challenged

- Olive oil n° 28
- Chocolate n° 16
- Cocoa powder n° 59

## Oil samples

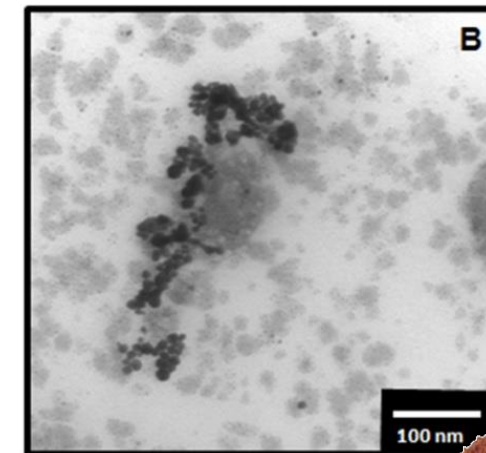
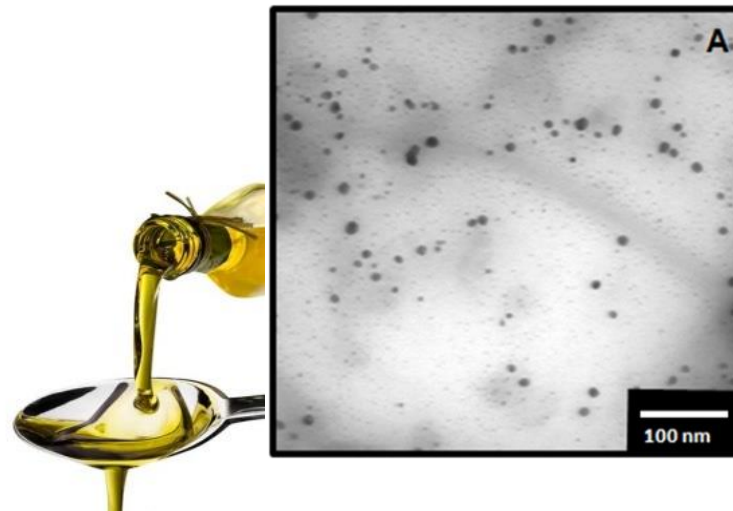


## Chocolate and cocoa samples



• Recoveries between 90 and 110 %

• Tocopherol fortification  
31.25-5000 mg L<sup>-1</sup> no AuNPs  
formation



# Metal nanoparticles (MNPs)

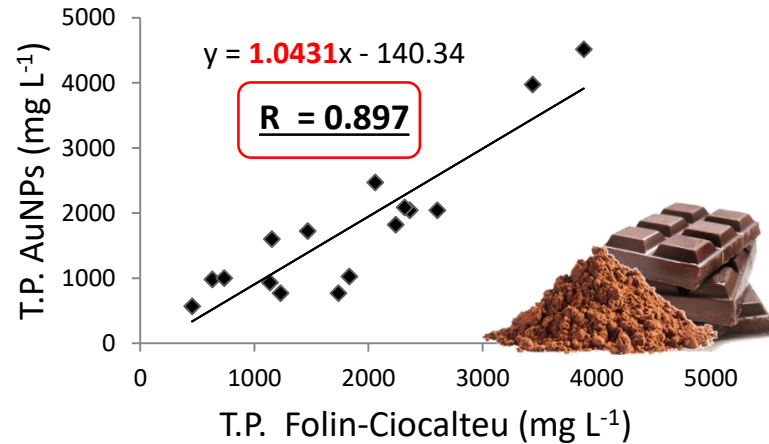
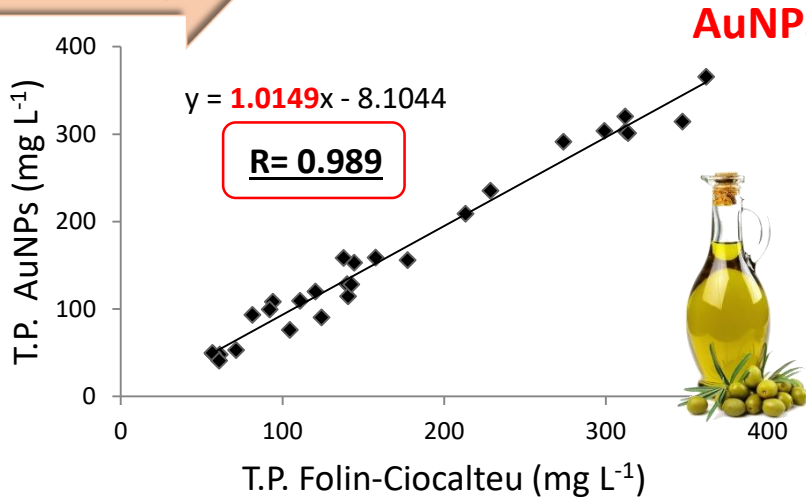
AuNPs  
Fat

AoC

Fat

Matrix Sample

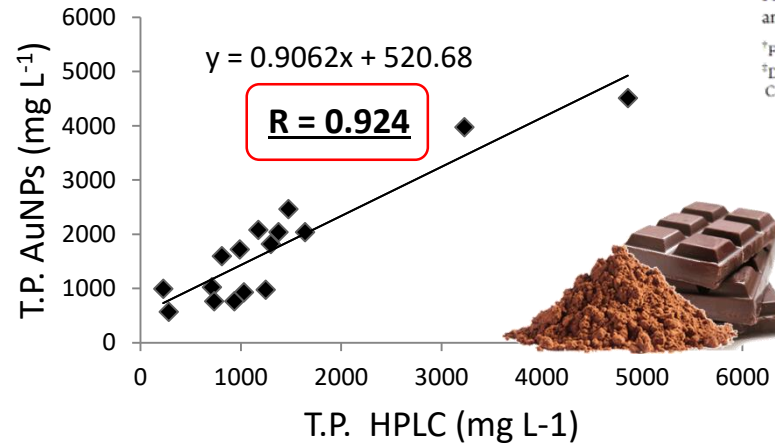
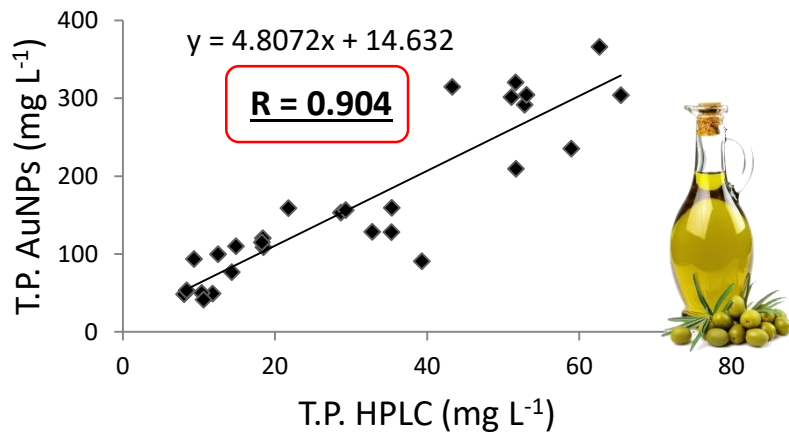
## AuNPS method vs. F.C. and HPLC-Uv/DAD (Olive n°28 and chocolate n°16 samples)



analytical  
chemistry

Article  
pubs.acs.org/ac

### AuNPS vs. HPLC



Gold Nanoparticles-based Extraction-Free Colorimetric Assay in Organic Media: An Optical Index for Determination of Total Polyphenols in Fat-Rich Samples

Flavio Della Pelle,<sup>†,‡</sup> Maria Cristina González,<sup>‡</sup> Manuel Sergi,<sup>†</sup> Michele Del Carlo,<sup>†</sup> Dario Compagnone,<sup>\*,‡</sup> and Alberto Escarpa<sup>\*,‡</sup>

<sup>†</sup>Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023 Teramo, Italy

<sup>‡</sup>Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Faculty of Biology, Environmental Sciences and Chemistry, University of Alcalá, E-28871 Alcalá de Henares, Madrid, Spain

## AgNPs-based AoC and flavanols content Evaluation

AgNPs  
RT

Polyphenols  
Sensitive  
Detection

- Sensitive AoC evaluation
- pH (13)
- T (**Room Temperature**)
- Sensitive (LOD  $\leq 0.4 \mu\text{M}$  gallic acid)

*Total assay time: 10 min*

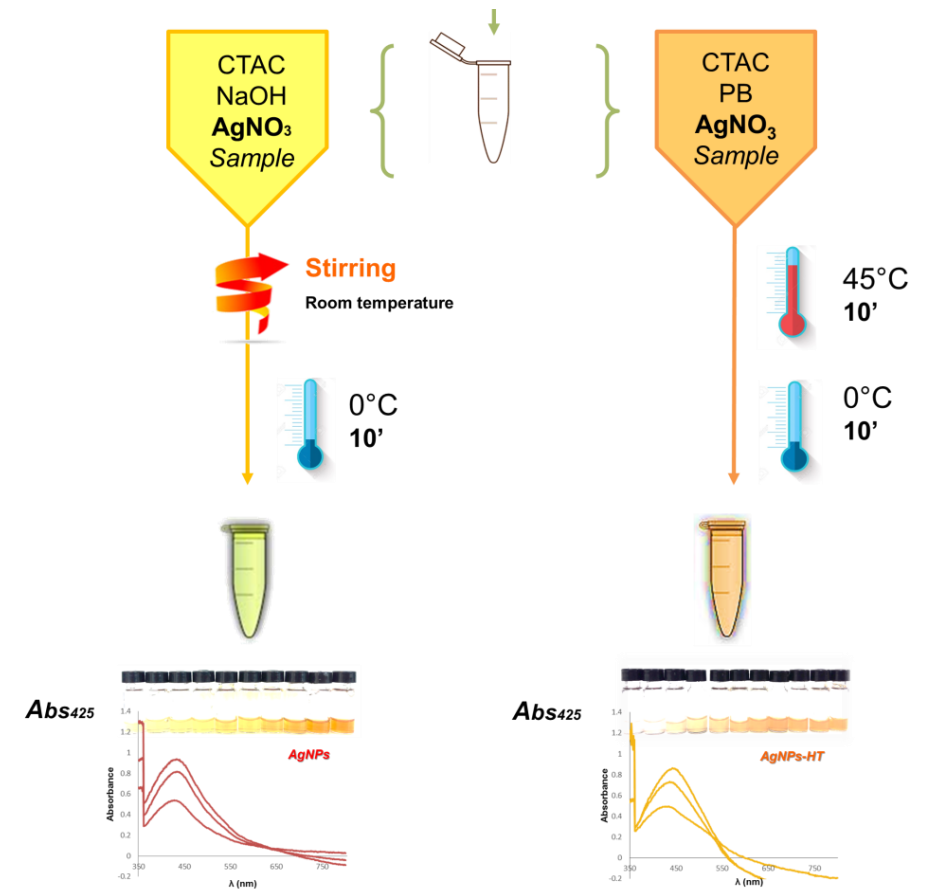
AgNPs  
HT

Polyphenols  
Class Selectivity

- Flavanols assessment
- pH (8,3)
- T (45°C)
- Sensitivity to the intrinsic antioxidant capacity

*Total assay time: 10 min*

### AgNPs-based strategies

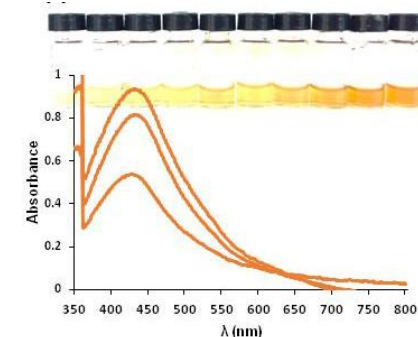
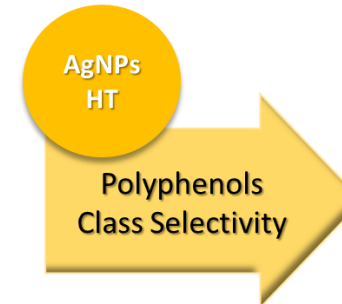
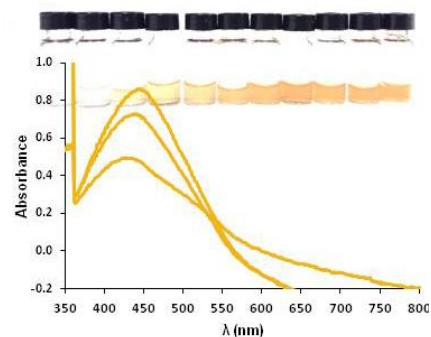
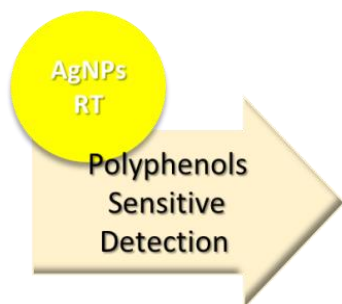


# Metal nanoparticles (MNPs)

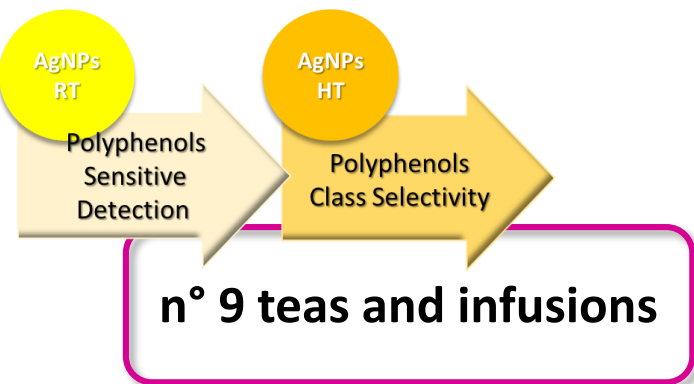
## AgNPs Polyphenol sensing... polyphenolic standards Reactivity study

Analytical parameters obtained by the polyphenol standards dose–response curve employing the two proposed AgNPs-based method.

Standard	AgNPs-RT			AgNPs-HT		
	Linear range μM	Equation	R <sup>2</sup>	Linear range μM	Equation	R <sup>2</sup>
Caffeic acid	1.5–12.5	$y = 0.029x + 0.191$	0.993	10–100	$y = 0.005x + 0.409$	0.996
Catechin	0.25–6	$y = 0.056x + 0.331$	0.991			
Catecol	1.5–30	$y = 0.010x + 0.371$	0.991	20–90	$y = 0.008x + 0.166$	0.993
Chlorogenic acid	3–25	$y = 0.018x + 0.284$	0.994			
Epicatechin	1–7.5	$y = 0.041x + 0.286$	0.991	20–200	$y = 0.003x + 0.365$	0.996
Epigallocatechin	0.5–7.5	$y = 0.044x + 0.315$	0.991			
Ferulic acid	10–125	$y = 0.002x + 0.303$	0.991	200–600	$y = 0.001x + 0.289$	0.998
Gallic acid	1–15	$y = 0.019x + 0.280$	0.991			
Kaempferol	5–65	$y = 0.006x + 0.266$	0.994	20–250	$y = 0.002x + 0.522$	0.999
Myricetin	1–6	$y = 0.064x + 0.223$	0.992	100–200	$y = 0.005x - 0.280$	0.991
Quercetin	1–12.5	$y = 0.048x + 0.164$	0.992	100–200	$y = 0.005x - 0.115$	0.993
Rutin	2–20	$y = 0.023x + 0.199$	0.993	30–90	$y = 0.007x + 0.289$	0.996
Trolox	1–20	$y = 0.018x + 0.385$	0.992			



# Metal nanoparticles (MNPs)



## AgNPs Polyphenol sensing... samples reactivity study



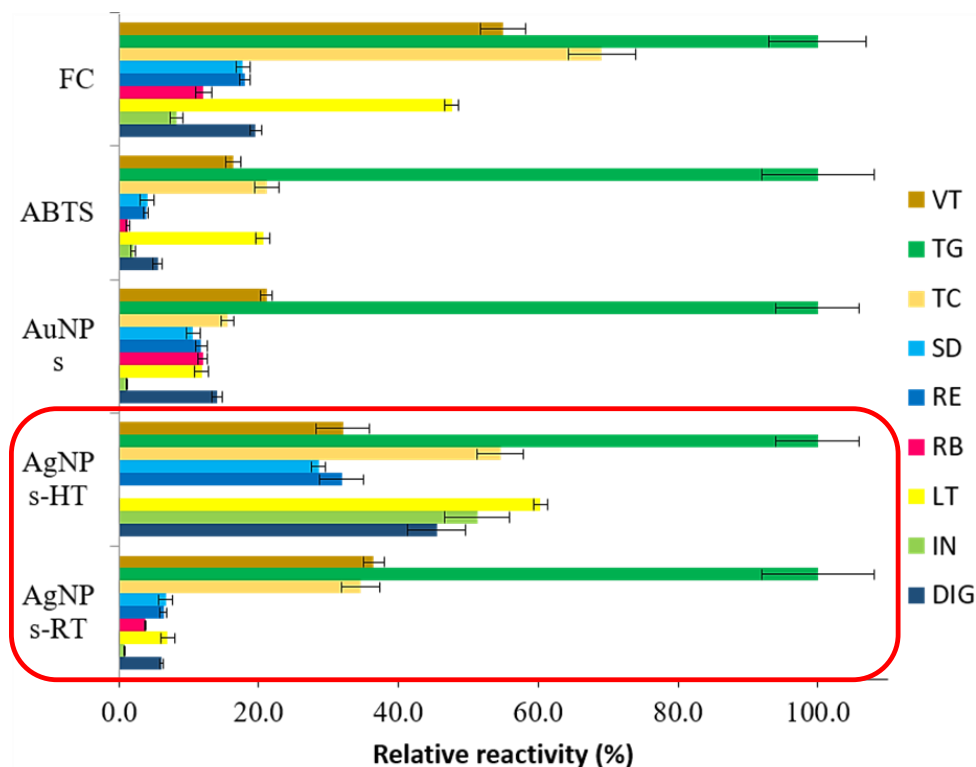
VT: Vanilla Tea  
TG: Green Tea  
TC: Classic Tea  
SD: sogni d'oro infused  
RE: Relax infused

RB: Rosa di bosco Infused  
LT: Lemon Tea  
IN: Finocchio infused  
DIG: Digestiva infused

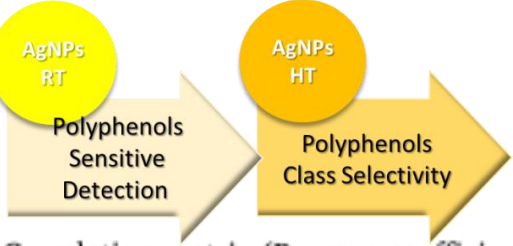
## AgNPs-RT, AgNPs-HT vs. F.C, ABTS and AuNPs



Method \ Sample	DIG		IN		LT		RB		RE		SD		TC		TG		VT	
	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)	(g Kg <sup>-1</sup> )	RSD (%)
AgNPs-RT	8.66	4	1.20	9	9.91	5	5.31	3	9.12	8	9.62	7	49.50	8	143.01	3	52.19	4
AgNPs-HT	11.10	9	12.52	9	14.73	5			7.78	10	6.98	14	13.33	6	24.42	7	7.82	12
AuNPs	18.63	5	1.52	7	15.64	2	15.86	5	15.58	7	14.03	5	20.56	6	132.35	3	27.95	4
ABTS	3.03	12	1.12	14	11.26	7	0.70	14	2.13	9	2.21	12	11.55	8	54.57	5	8.92	7
FC	5.98	4	2.51	11	14.54	3	3.70	10	5.51	4	5.42	5	21.10	7	30.54	8	16.79	6



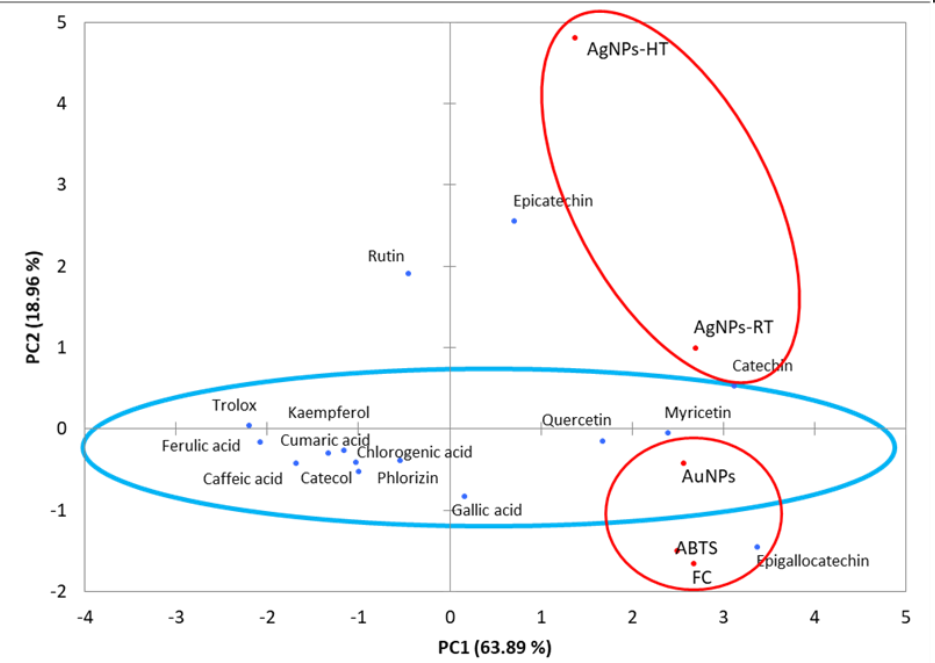
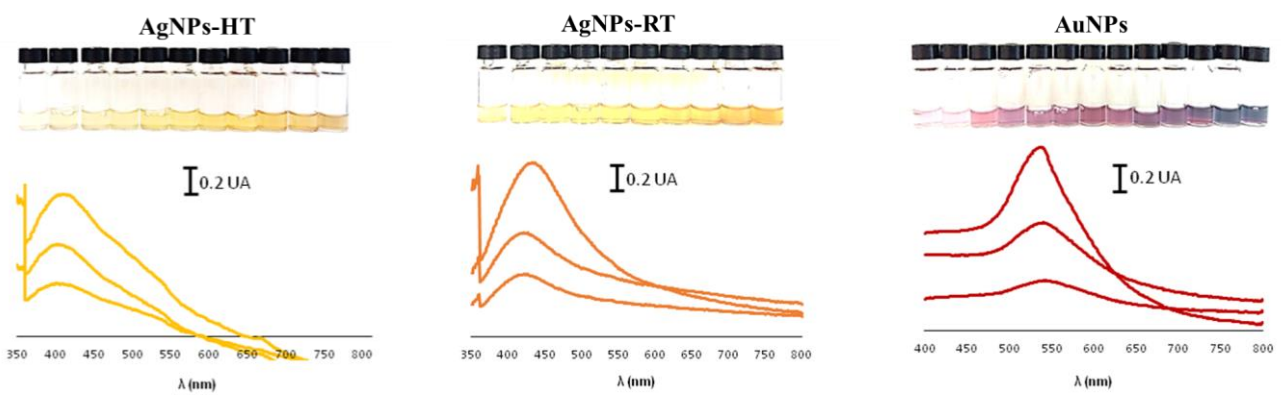
# Metal nanoparticles (MNPs)



AgNPs-RT, AgNPs-HT vs. F.C, ABTS and AuNPs

Correlation matrix (Pearson coefficient) for all the antioxidant capacity methods tested.

	ABTS		FC		AgNPs-HT		AgNPs-RT		AuNPs	
ABTS	1	(p = 0)	0.876	(p = 0.002)	0.891	(p = 0.001)	0.956	(p = 0.000)	0.977	(p = 0.000)
FC	0.876	(p = 0.002)	1	(p = 0)	0.733	(p = 0.025)	0.913	(p = 0.001)	0.801	(p = 0.009)
AgNPs-HT	0.891	(p = 0.001)	0.733	(p = 0.025)	1	(p = 0)	0.770	(p = 0.015)	0.826	(p = 0.006)
AgNPs-RT	0.956	(p = < 0.0001)	0.913	(p = 0.001)	0.770	(p = 0.015)	1	(p = 0)	0.950	(p = < 0.0001)
AuNPs	0.977	(p = < 0.0001)	0.801	(P = 0.009)	0.826	(p = 0.006)	0.950	(p = < 0.0001)	1	(p = 0)



# Metal nanoparticles (MNPs)

## Polyphenol UHPLC–MS/MS evaluation comparison with the AgNPs-HT assay

Sample Standard	DIG (g Kg <sup>-1</sup> )	IN (g Kg <sup>-1</sup> )	LT (g Kg <sup>-1</sup> )	RB (g Kg <sup>-1</sup> )	RE (g Kg <sup>-1</sup> )	SD (g Kg <sup>-1</sup> )	TC (g Kg <sup>-1</sup> )	TG (g Kg <sup>-1</sup> )	VT (g Kg <sup>-1</sup> )
Caffeic acid	3.36E-02*	2.42E-03	3.19E-03	1.56E-02	3.93E-02	3.44E-02	2.19E-04	<LOQ	6.48E-04
Catechin	<LOQ**	<LOQ	1.00E-01	1.86E-03	1.54E-03	1.29E-03	2.65E-01	8.61E-01	4.91E-01
Catecol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Chlorogenic acid	1.71E-01	2.05E-01	5.74E-02	2.44E-01	5.36E-01	5.09E-01	1.25E-01	8.11E-02	5.68E-02
Cumaric acid	4.69E-03	1.77E-04	<LOQ	<LOQ	1.45E-03	6.12E-03	1.03E-03	<LOQ	3.07E-04
Epicatechin	<LOQ	<LOQ	9.64E-02	<LOQ	4.62E-03	1.48E-01	2.64E-01	9.93E-01	5.39E-01
Epigallocatechin	<LOQ	<LOQ	2.09E-01	<LOQ	<LOQ	<LOQ	4.19E-01	2.28E+01	7.48E-01
Ferulic acid	1.27E-02	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Gallic acid	7.42E-03	<LOQ	6.54E-01	3.23E-02	<LOQ	<LOQ	9.17E-01	4.74E-01	8.34E-01
Kaempferol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Myricetin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Phlorizin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Quercetin	4.07E-02	<LOQ	<LOQ	5.74E-02	<LOQ	3.07E-03	<LOQ	<LOQ	<LOQ
Rutin	2.49E-01	<LOQ	<LOQ	<LOQ	<LOQ	1.92E-02	<LOQ	<LOQ	<LOQ
Trolox	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Total phenols</b>	<b>2.06E+00</b>	<b>2.08E-01</b>	<b>1.53E+00</b>	<b>3.79E-01</b>	<b>2.38E+00</b>	<b>3.52E+00</b>	<b>2.94E+00</b>	<b>2.61E+01</b>	<b>3.49E+00</b>
<b>Phenols fraction</b>	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
<b>Flavonols (%)</b>	56.9	0.0	53.3	23.1	19.4	41.0	64.4	97.9	72.9
<b>o-diphenols (%)</b>	61.4	99.9	100.0	100.0	80.4	76.6	100.0	100.0	98.3
<b>m-phenols (%)</b>	38.6	0.1	0.0	0.0	19.2	23.4	0.0	0.0	1.7

### Flavanols content trend

**UHPLC-MS/MS** TG > VT > TC > DIG > LT > SD > RB > RE > IN

**AgNPs-HT** TG > VT > TC > DIG > LT > SD > RB > RE > IN

**VT:** Vanilla Tea

**TG:** Green Tea

**TC:** Classic Tea

**SD:** sogni d'oro infused

**RE:** Relax infused

**RB:** Rosa di bosco Infused

**LT:** Lemon Tea

**IN:** Finocchio infused

**DIG:** Digestiva infused

Food Chemistry 256 (2018) 342–349



ELSEVIER

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: [www.elsevier.com/locate/foodchem](http://www.elsevier.com/locate/foodchem)



Simple and rapid silver nanoparticles based antioxidant capacity assays: Reactivity study for phenolic compounds

Flavio Della Pelle, Annalisa Scroccarello, Manuel Sergi, Marcello Mascini, Michele Del Carlo, Dario Compagnone\*

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023 Teramo, Italy



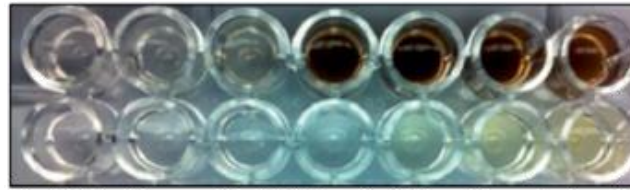
# Metal nanoparticles (MNPs)

Nano Ceria

Polyphenols evaluation

Optimization

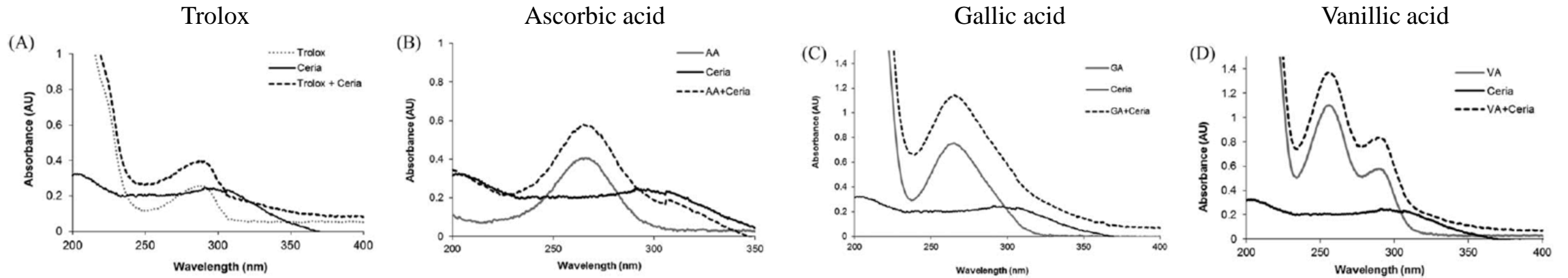
[CeO<sub>2</sub>] 0.0025, 0.005, 0.01, 0.1, 1, 2, and 4%



Caffeic acid (0,45 mM) reacted [CeO<sub>2</sub>]

[CeO<sub>2</sub>]= 4%

Uv-vis spectra of ceria nanoparticles dispersion (13 ppm) in the presence and absence of selected antioxidants.



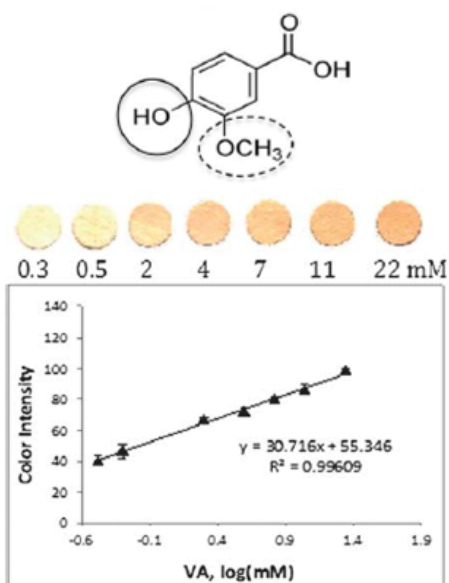
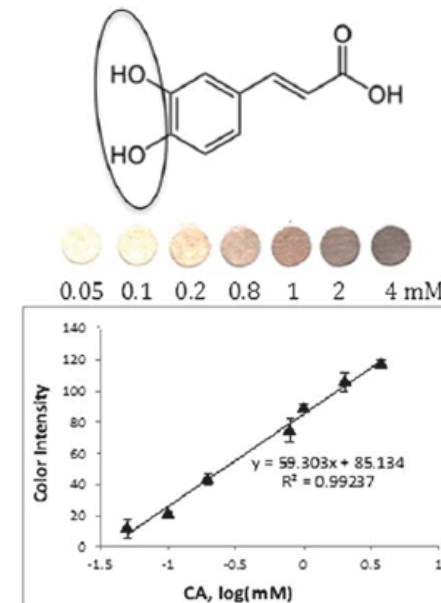
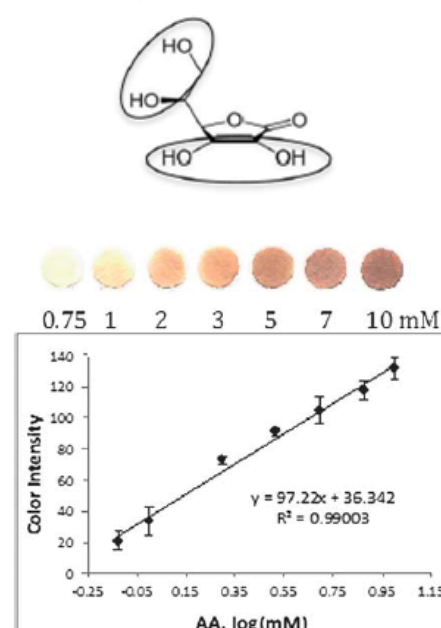
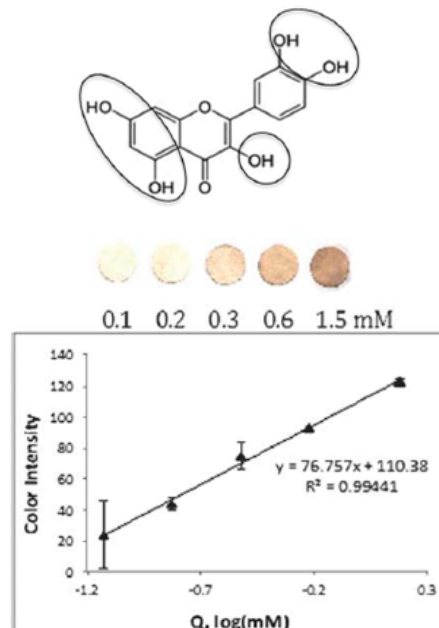
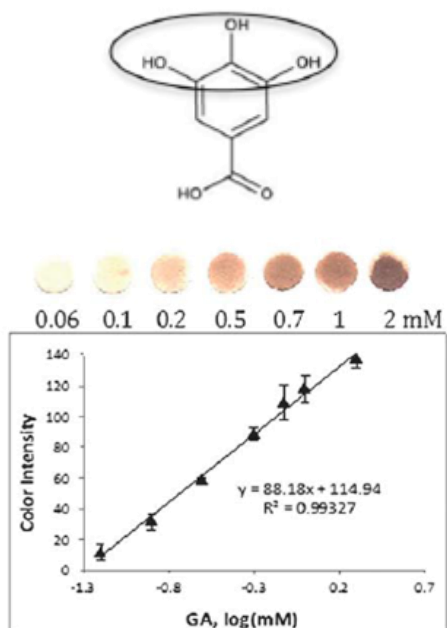
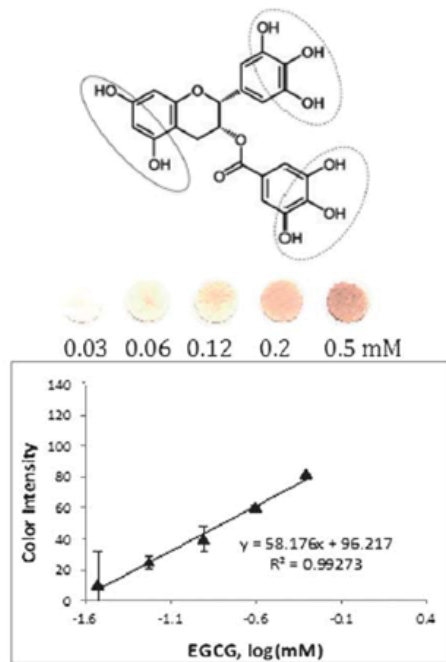
to paper support



From dispersed system



# Metal nanoparticles (MNPs)



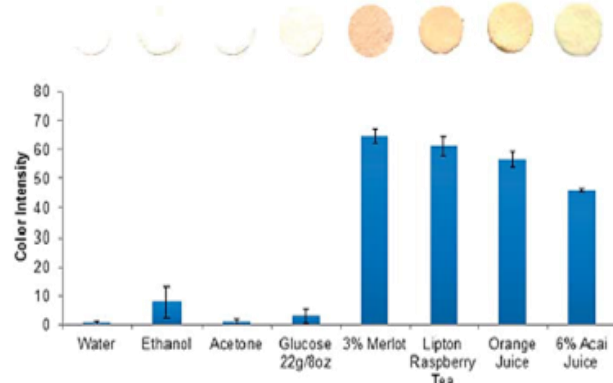
## Tested interfering compounds

Common lab solvent:

- water,
- ethanol,
- acetone

Common sugar presents in:

- juice,
- wine,
- commercial teas



## Analyst

PAPER

Cite this: DOI: 10.1039/c2an36205h

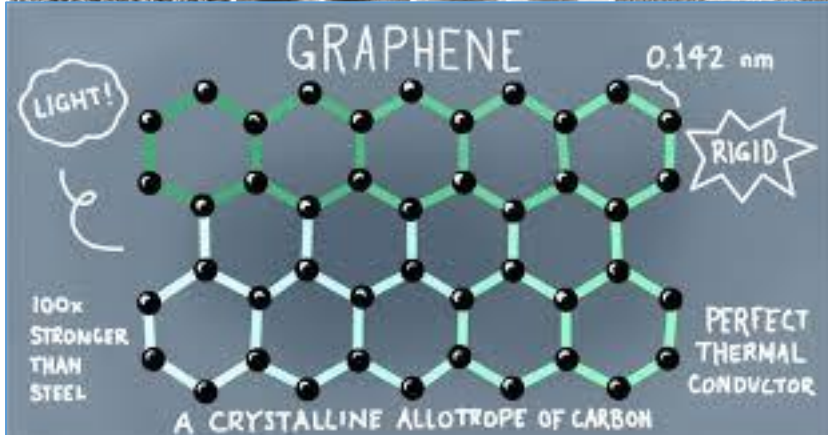
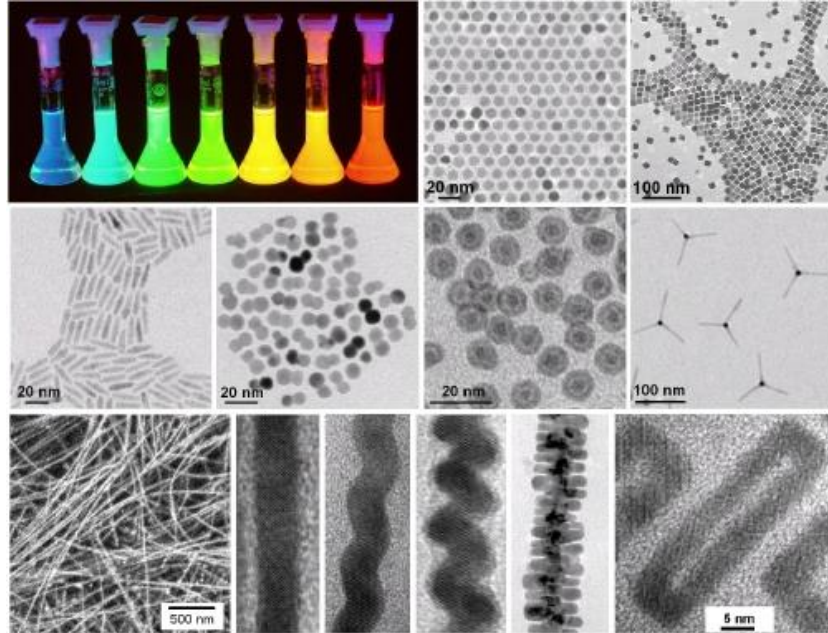
RSC Publishing

[View Article Online](#)  
[View Journal](#)

## Portable ceria nanoparticle-based assay for rapid detection of food antioxidants (NanoCerac)

Erica Sharpe, Thalia Frasco, Daniel Andreescu and Silvana Andreescu\*

# Nanomaterials employed in electrochemical sensor

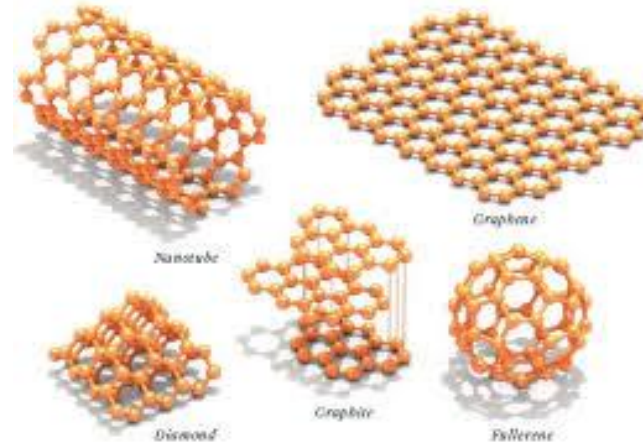


## Carbon based nanomaterials:

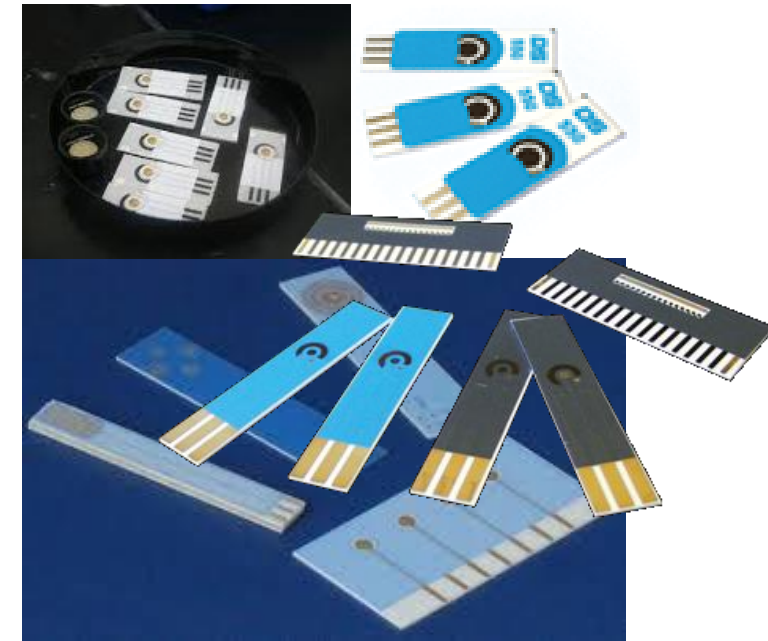
- Nanotubes
- Fullerenes
- Graphene
- Etc...

## Nanoparticles:

- Metal nanoparticles
- Metal Oxide nanoparticles

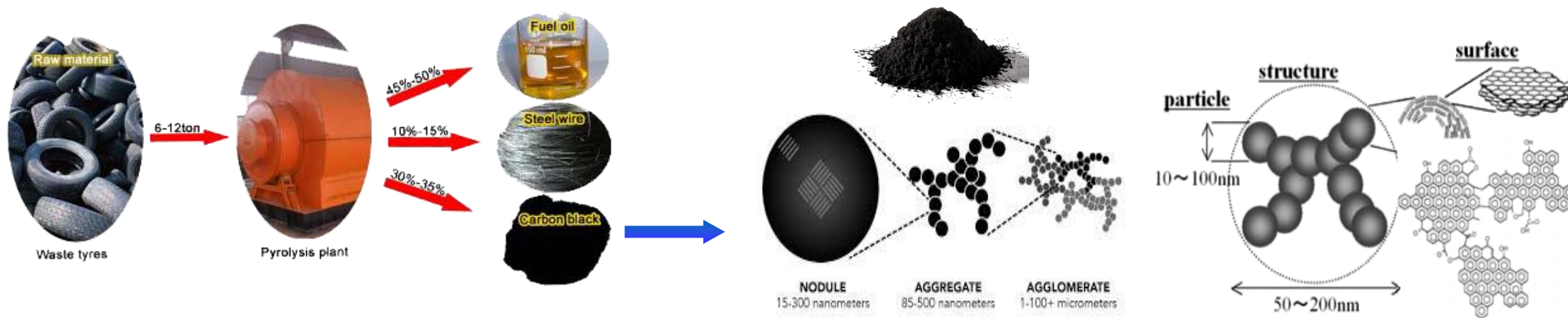


## Screen printed electrodes



# Carbon based nanomaterials (*Carbon Black, CB*)

**Carbon black** is a material produced by the incomplete combustion of heavy petroleum products. It is mainly used as a reinforcing filler in tires and other rubber products. In plastics, paints, and inks, carbon black is used as a color pigment



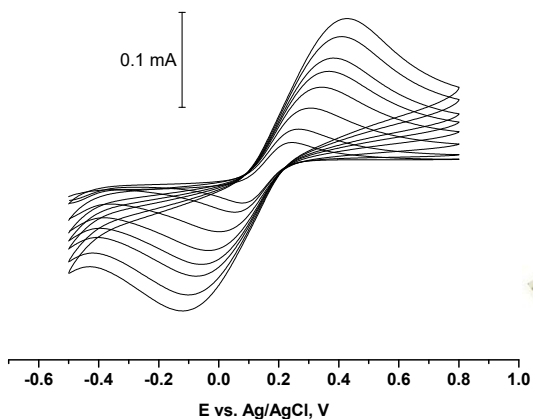
Electrocatalysis	➔	Selectivity
High surface	➔	Sensitivity
Resistance to fouling	➔	Reproducibility
Faster eletron transfer	➔	Improving separation performance

## ***CB compared with other nanomaterials:***

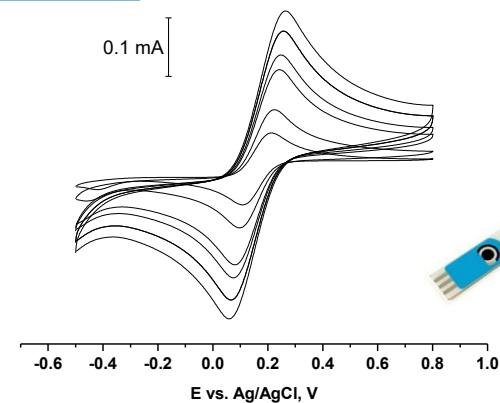
**Very low cost**  
**No synthesis**  
**No impurities due to synthesis**  
**Easily dispersible**  
**Large number of defect sites**

# SPE-CBNPs electrochemical behaviour for ferricyanide

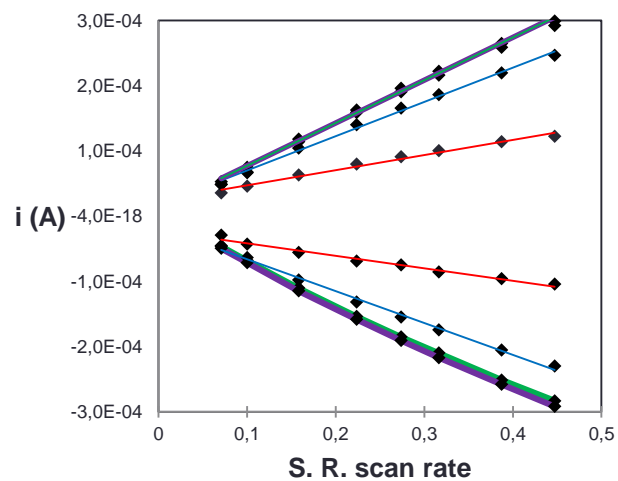
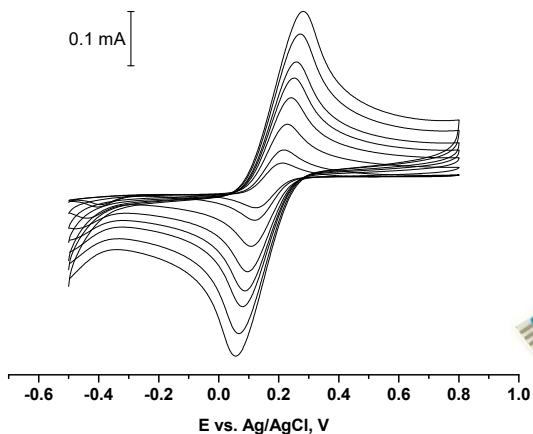
**Carbon SPE**



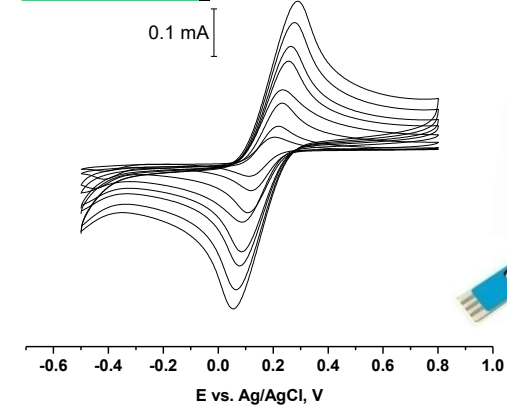
**Graphene/Carbon SPE (DS110-GPH)**



**Carbon-CB SPE**



**Graphene/Carbon-CB SPE (DS110-GPH)**



CB modified SPE demonstrates a better electron transfer

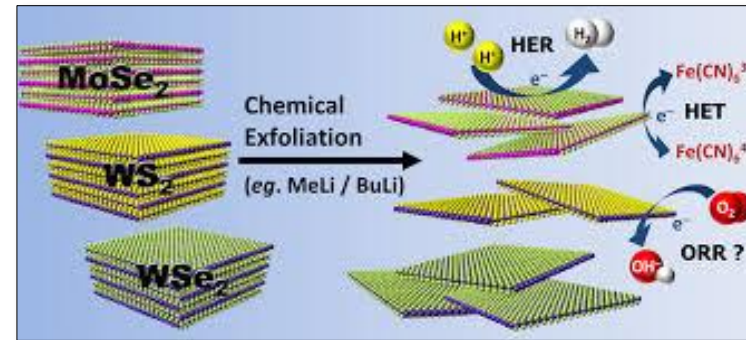
# Graphene-like nanomaterials

## Graphene-like two-dimensional layered nanomaterials, transition metal dichalcogenides (TMDs)

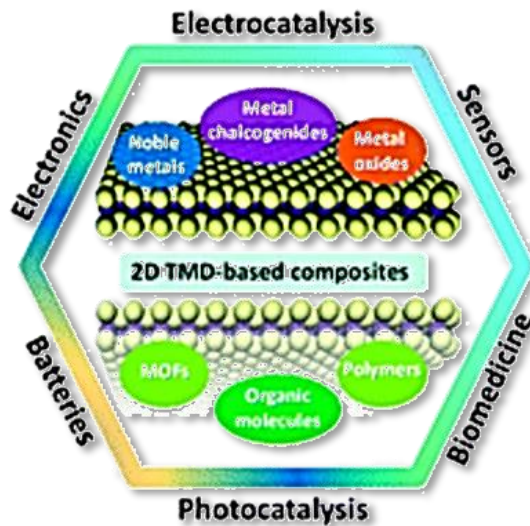
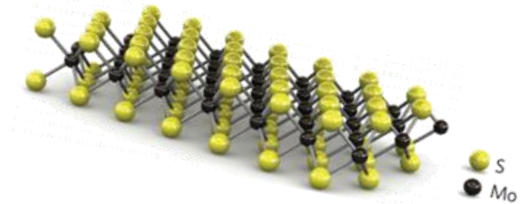
**$MX_2$**  ----- **X = Chalcogen**

**M = Transition Metal**

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo



Eng, A. Y. S., Ambrosi, A., Sofer, Z., Simek, P., & Pumera, M. (2014). Electrochemistry of transition metal dichalcogenides: strong dependence on the metal-to-chalcogen composition and exfoliation method. *ACS nano*, 8(12), 12185-12198.

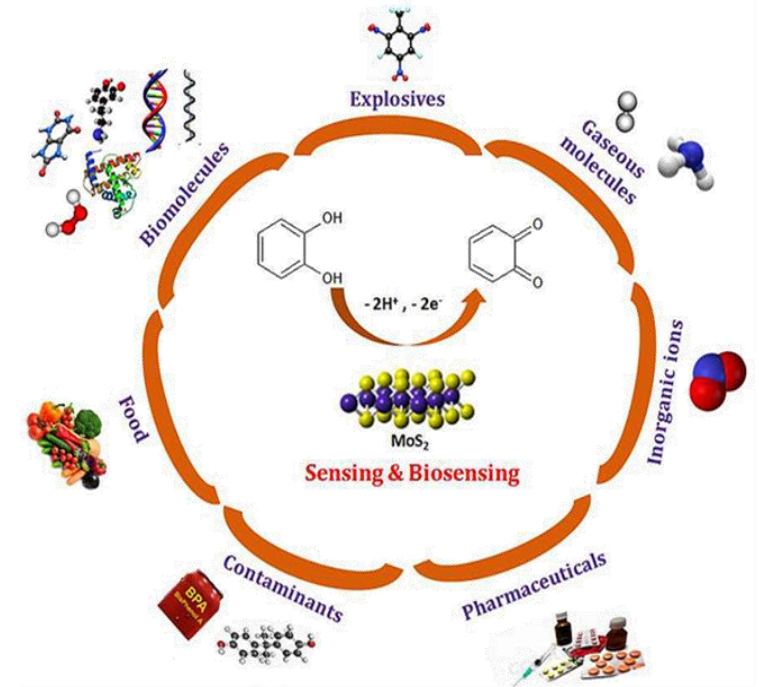
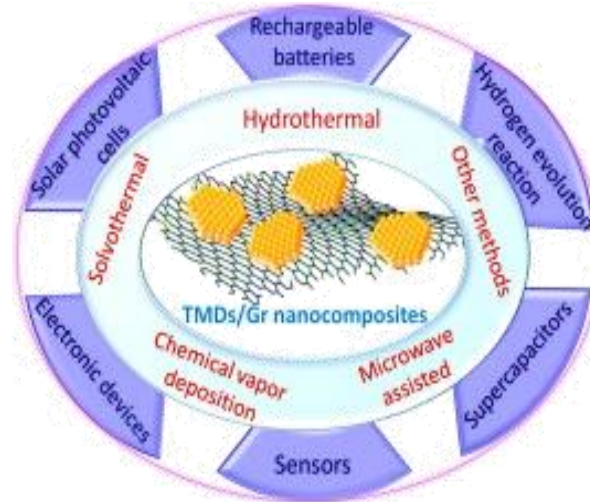
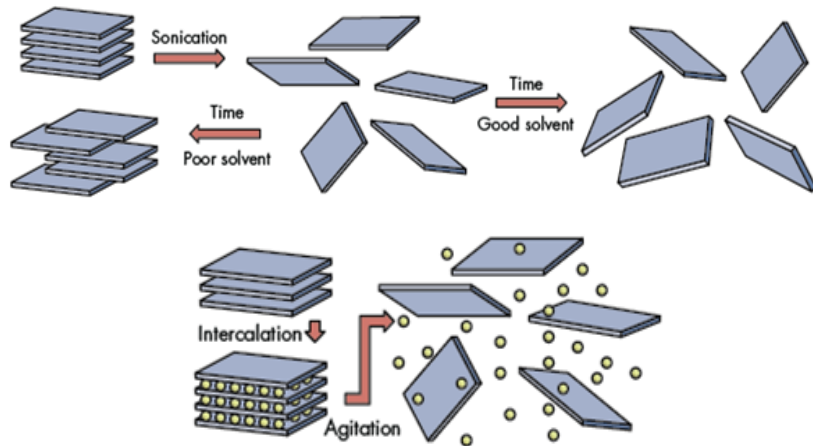


- TMDs nanosheets Easy to prepare
- Unique electrical, optical, and mechanical properties
- Large surface area, low cost, stability
- Metallic and semi-conducting electrical capabilities
- Widely employed in hydrogen evolution reaction (HER) and energy storage
- Few applications in (bio)sensors employed in food analysis
- Tunable electrocatalytic properties /intercalatable morphologies

# Graphene-like nanomaterials

## TMDs and TMDs-based nanocomposite for sensor and biosensors

2D NMs can form heterostructures with layers of varied materials and with a thickness of one or two atoms, and thus synergistically improve their physicochemical properties.



**Exfoliation using intercalating materials/  
appropriate solvent**  
(single- or few-layer TMDs nanosheets)

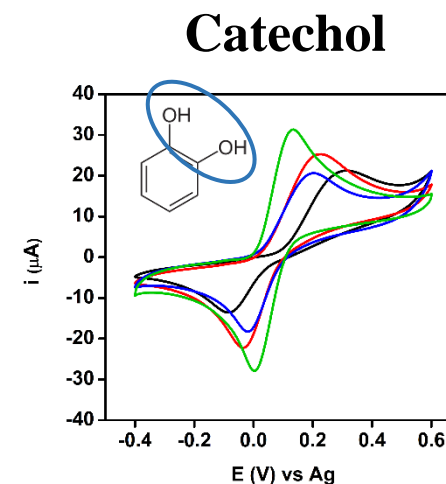
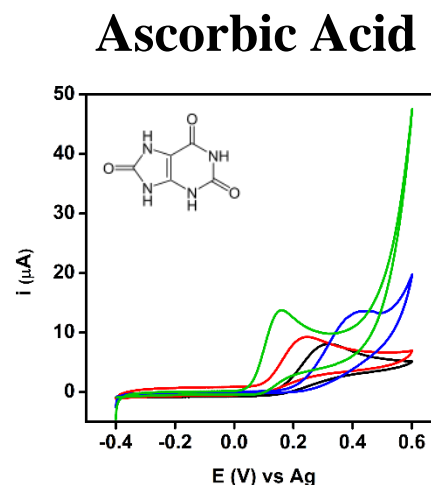
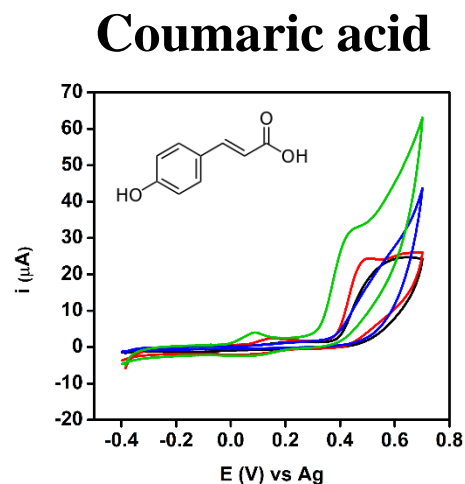
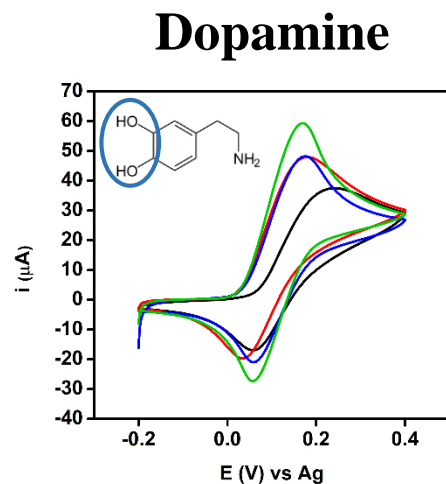
### TMDs-based nanocomposites/ Hybrid nanoarchitectures

These strategies avoiding restacking, narrow potential window, low conductivity, fouling, etc.  
**improving the general electrochemical performance**

*TMDs-based sensors and biosensors growing field and holds great promise*

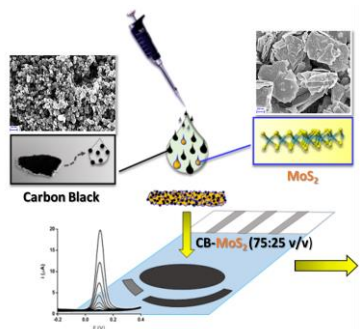
# Graphene-like nanohybrids materials

Electrochemical response towards common electroactive species  
Interesting response for o-diphenols



— SPE  
— CB  
— MoS<sub>2</sub>  
— CB-MoS<sub>2</sub>

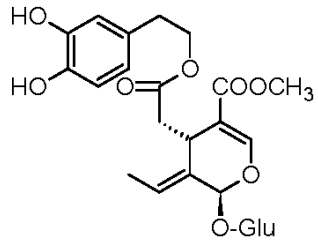
CVs of 1 mmol L<sup>-1</sup> of each compound at a scan rate of 50 mV s<sup>-1</sup>.



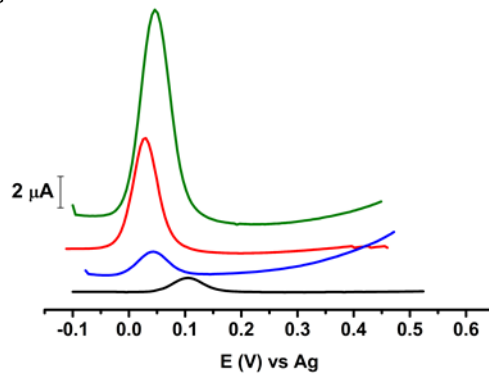
- Dopamine and Catechol showed an improvement in the peak-to-peak separation and increased peak intensities.
- Coumaric acid and ascorbic acid showed a negative shift and improved peak intensities.
- SPE-CB-MoS<sub>2</sub> anodic peak intensity decrease was in the  $\leq 2\%$  and  $\leq 10\%$  for Catechol/Dopamine and Uric acid/Coumaric acid, respectively, after 10 scans

# Graphene-like nanohybrids materials

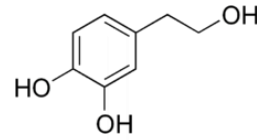
## A case study: olive oil ortho-phenols



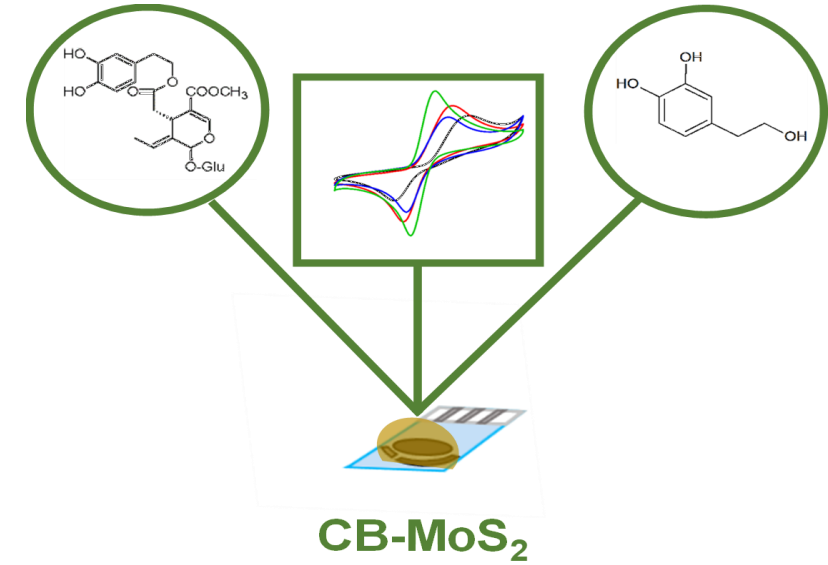
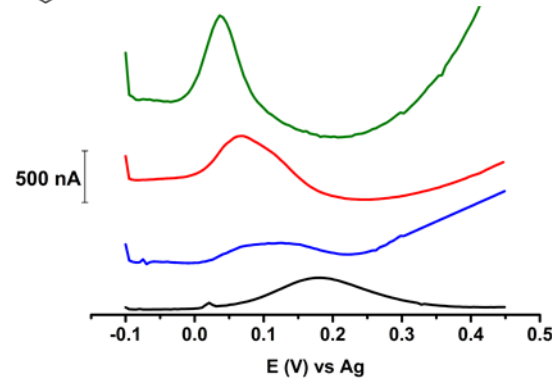
**OLEUROPEIN**



— SPE  
— CB  
— MoS<sub>2</sub>  
— CB-MoS<sub>2</sub>



**HYDROXYTYROSOL**

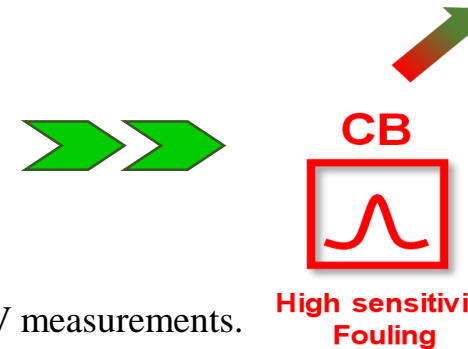
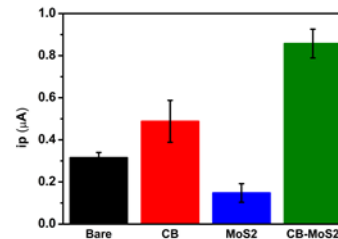
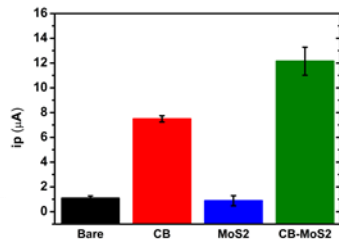


**CB-MoS<sub>2</sub>**



**High sensitivity Antifouling**

- Ortho-phenols are the main contributors to the antioxidant capacity of Olive Oil phenolic fraction.
- An increased oxidation current was observed for both o-diphenols in the modified electrodes



**High sensitivity Fouling**

**Low sensitivity Antifouling**

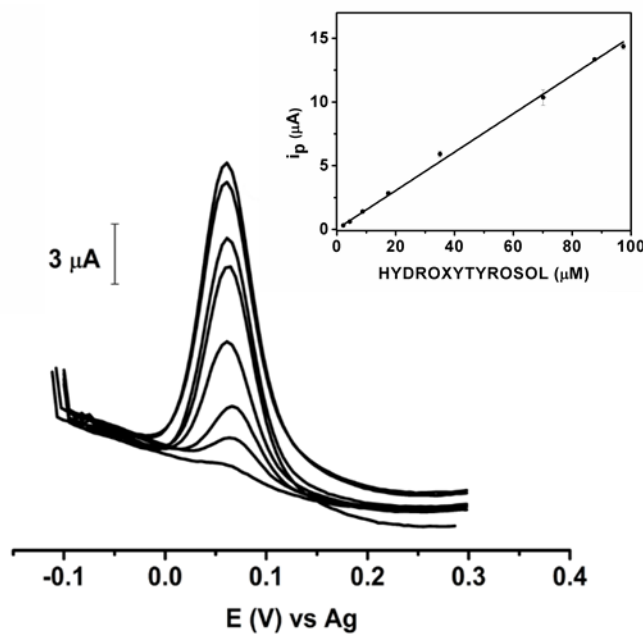
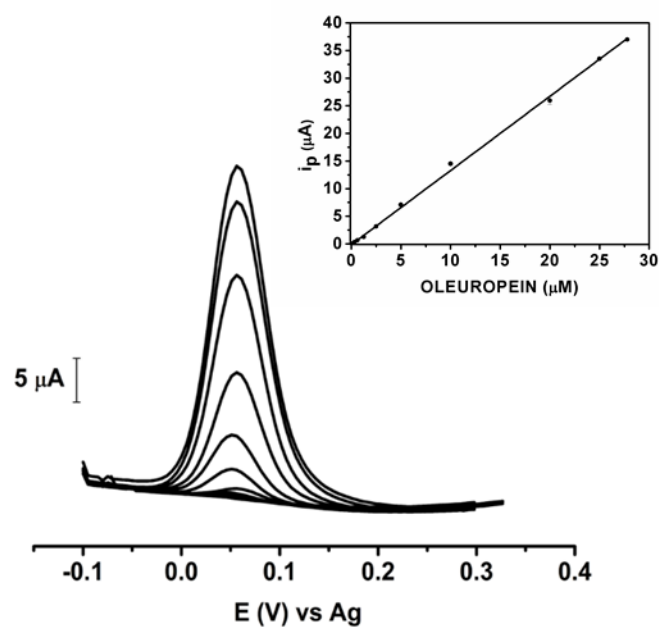
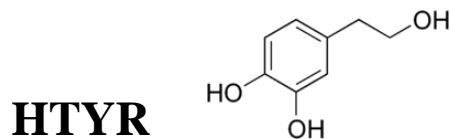
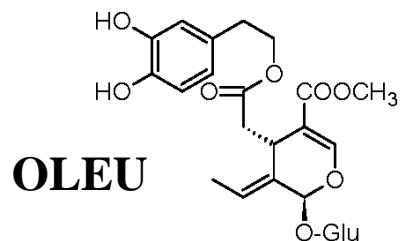
Fouling Effect was evaluated as the retained peak intensity after 10 consecutives DPV measurements.

The obtained values: 38% for Bare, **53% for CB**, 84% for MoS<sub>2</sub> and 86% for CB-MoS<sub>2</sub> modified SPE for OLEU



# Graphene-like nanohybrids materials

## Analytical performance towards olive oil ortho-phenols (differential pulse voltammetry)



	OLEU	HTYR
LOD ( $\mu\text{M}$ )	0.12	1.06
LOQ ( $\mu\text{M}$ )	0.32	2.20
Linear range ( $\mu\text{M}$ )	0.39-28	3.54-100
$R^2$	0.997	0.991
Reproducibility (RSD) (n=5)	9%	8%

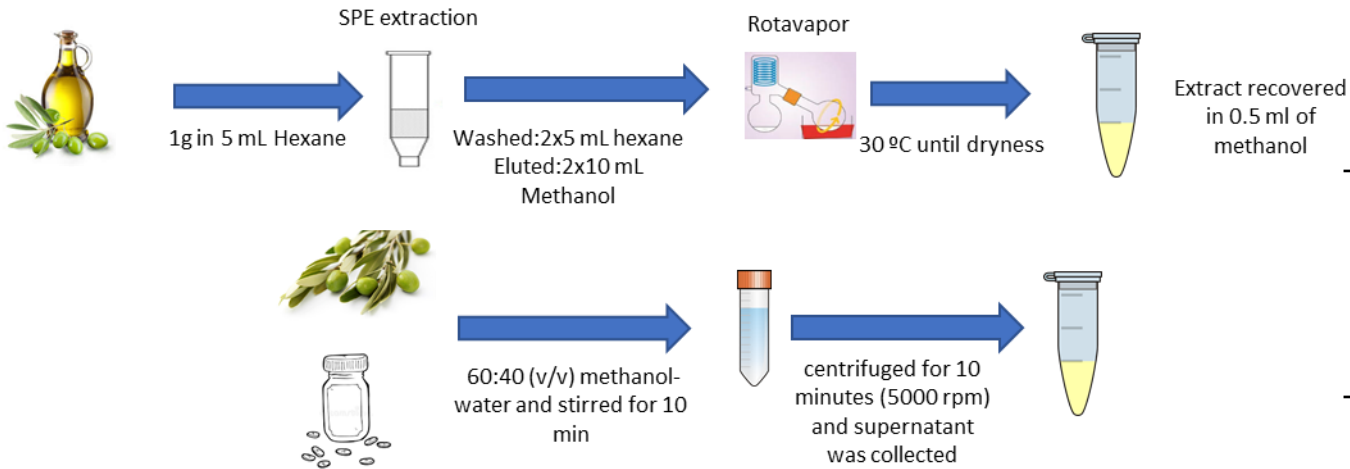
### Regression equations

$$i_p(\mu\text{A}) = -0.05(\pm 0.02) + 1.33(\pm 0.02) [\text{OLEU}](\mu\text{M})$$

$$i_p(\mu\text{A}) = 0.041(\pm 0.007) + 0.151(\pm 0.002) [\text{HTYR}](\mu\text{M})$$

# Graphene-like nanohybrids materials

## Sample treatment and analysis



## Recoveries in extracts

Matrix	OLEU eq (ppm) Found in the extract	OLEU (ppm) added	OLEU eq (ppm) found	Recovery (%)
Supplement	1.21±0.09	1	2.11±0.07	94±4
		3	4.15±0.29	98±7
		1	1.39±0.18	103±7
Olive Leaf	0.38±0.14	3	3.32±0.24	95±9
		1	1.40±0.07	108±6
Olive Oil	0.32±0.06	3	2.95±0.30	98±8

For recoveries calculation this formula has been employed:  $[(\text{Oleuropein concentration obtained with fortified sample} - \text{Oleuropein concentration obtained with unfortified sample}) / \text{Oleuropein concentration added}] * 100$

## Results obtained by sensor and HPLC-UV

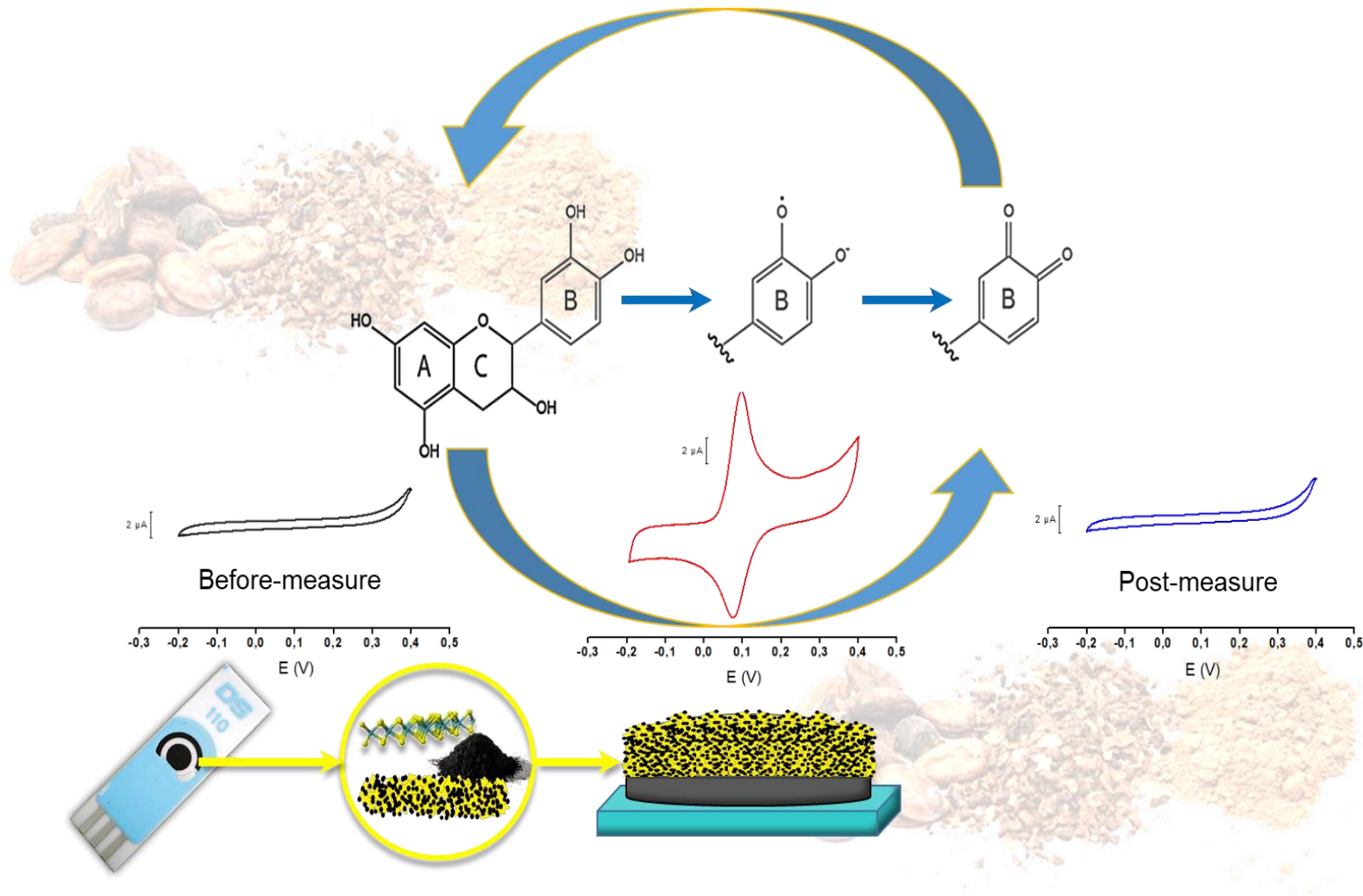
Sample	CB-MoS <sub>2</sub> SPE		HPLC-UV		
	Oleuropein eq. (mg Kg <sup>-1</sup> )	RSD (%)	o-diphenols (mg Kg <sup>-1</sup> )	RSD (%)	RE (%)
Dietary Supplement	5708±562	10	5534±277	5	7%
Olive Leaf 1	1286±55	4	1302±91	7	-1%
Olive Leaf 2	1193±97	8	1007±50	5	18%
Olive Oil 1	129±16	13	115±2	2	12%
Olive Oil 2	156±15	12	164±18	11	-4%
Olive Oil 3	45±3	7	36±6	15	15%

→ r=0.995

\*Data are reported as mean±standard deviation \*\*RSD=Relative Standard deviation\*\*\*RE=Relative Error

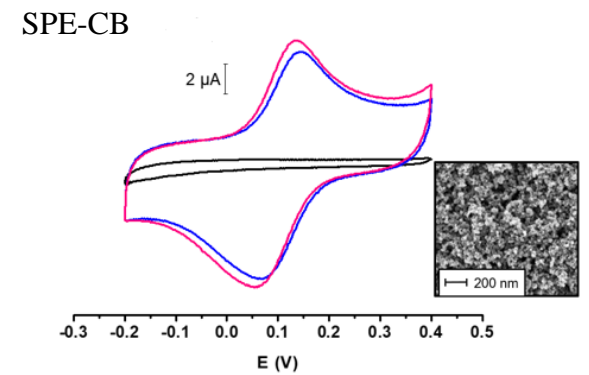
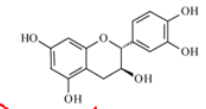
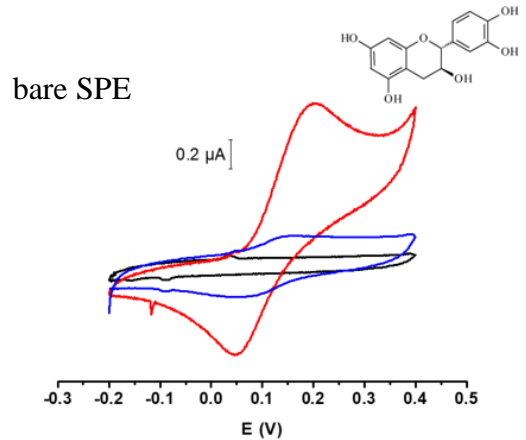
# Graphene-like nanohybrids materials

## A case study: Cocoa polyphenols

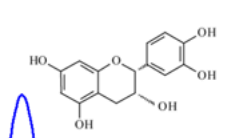
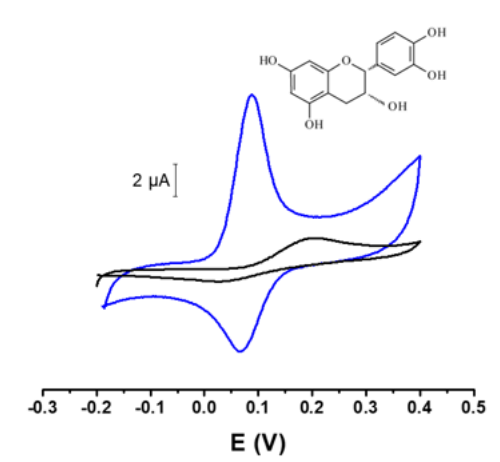


# (4) Graphene-like nanohybrids materials

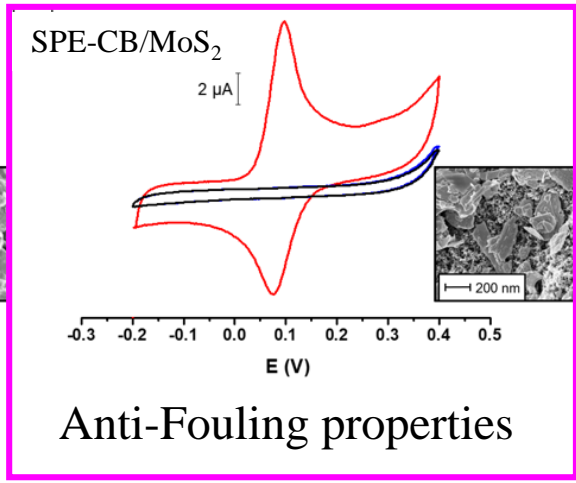
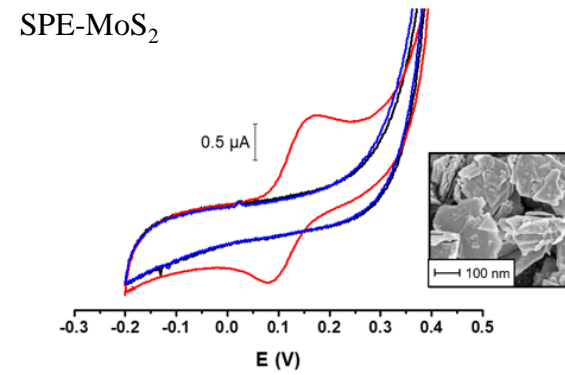
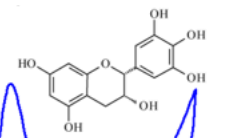
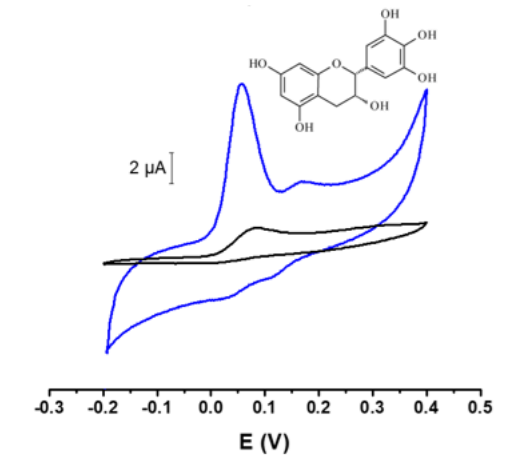
## CATECHIN



## EPICATECHIN

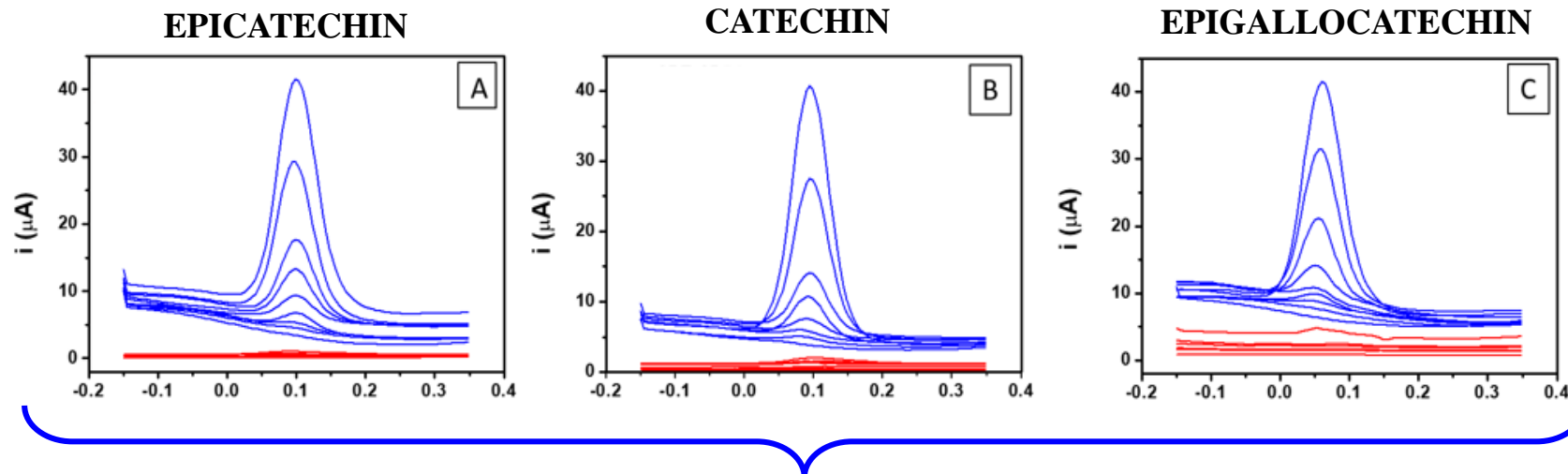


## EPIGALLOCATECHIN

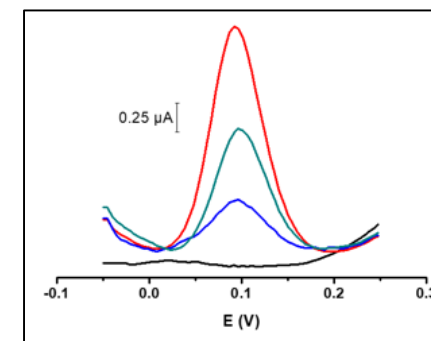


# (5) Graphene-like nanohybrids materials

## Standard calibration curve



## Fortified cocoa samples

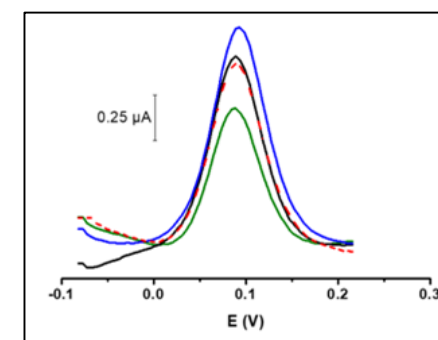


- + 0,25 μM catechin
- + 0,5 μM catechin
- Cocoa mix

Analytical characteristics of the SPE-CB/MoS<sub>2</sub> sensor employed for CT, EP, and EG detection.

	Linear Range (μmol L <sup>-1</sup> )	R <sup>2</sup>	Sensitivity (μA L μmol <sup>-1</sup> )	LOD (μmol L <sup>-1</sup> )
CT	0.1-25	0.998	1.12	0.18
EP	0.1-25	0.998	1.18	0.17
EG	0.1-25	0.998	1.10	0.18

<sup>1</sup>LODs were calculated as  $3\sigma/\text{slope}$  ratio, where  $\sigma$  is the standard deviation of the mean value for 10 voltammograms of the blank. Analytical characteristics calculated using the mean value of three calibration curves.

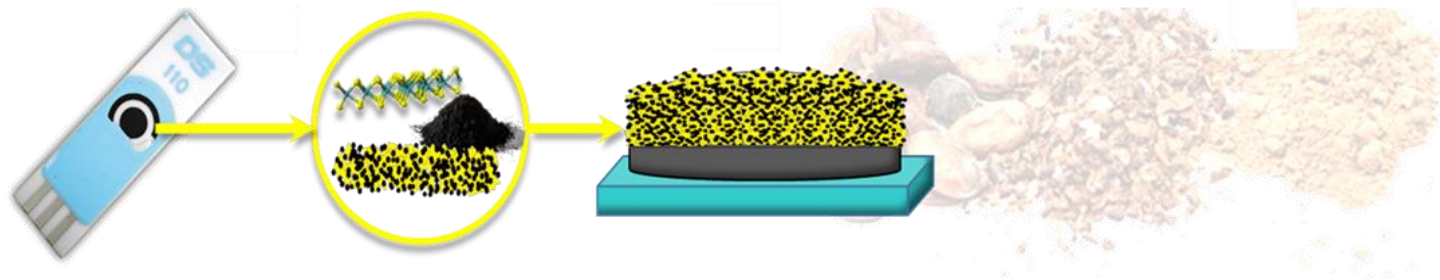
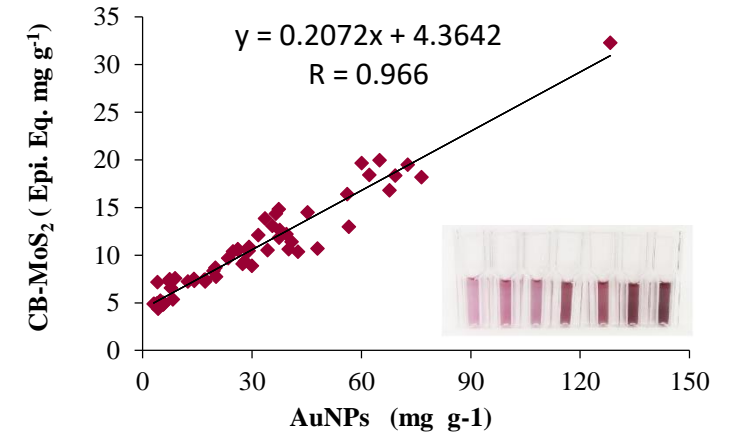
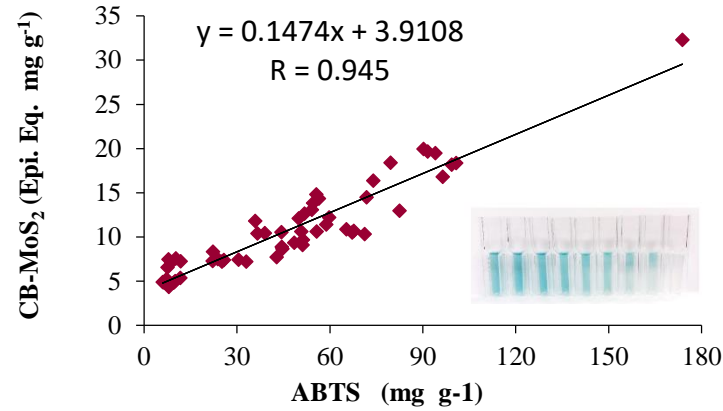
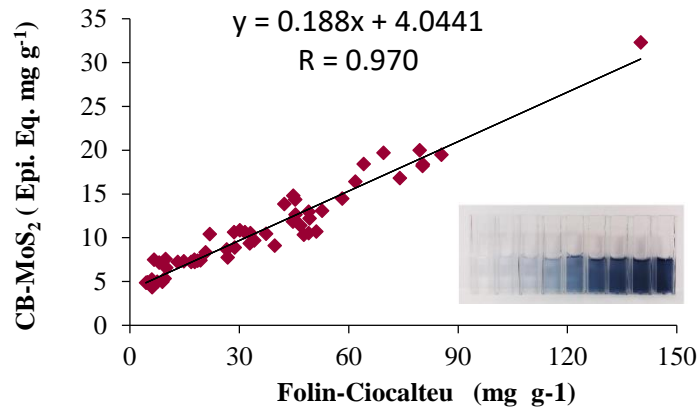


- Low polyphenols content
- Medium polyphenols content
- High polyphenols content
- - - n= 5 repetition after n° 59 cocoa measurement



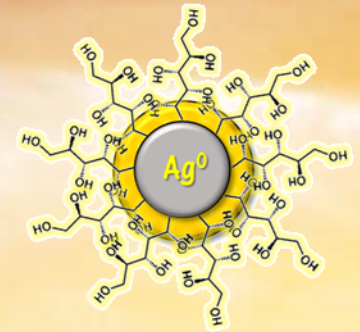
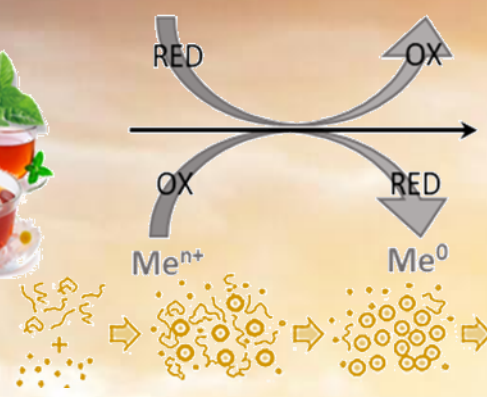
# Graphene-like nanohybrids materials

## Data correlation Optical assay vs. Electrochemical n= 59 sample



# *Conclusions*

- *The use of MNPs with optical detection, allows the evaluation of TP and/or AOC in a rapid way and can be alternative to the most used methods. The main advantage relies on the possibility, for some of the developed assay, to work without extraction from the samples (e.g., for olive oil) or with simplified assay based on visual assessment (e.g. on paper).*
- *The use of electrochemical sensors and sensing strategies, alternative to classical methods can be of great value for the sensitivity and assessment of different classes of polyphenols (i.e., o-diphenols vs. monophenols) giving important information about foods stability (shelf-life). The 'tunable' and unique features of nanomaterials and the possibility to combine different types of nanomaterials give more options and possible advantages over existing methods; particularly, increased sensitivity, selectivity and long term stability of the sensing systems.*



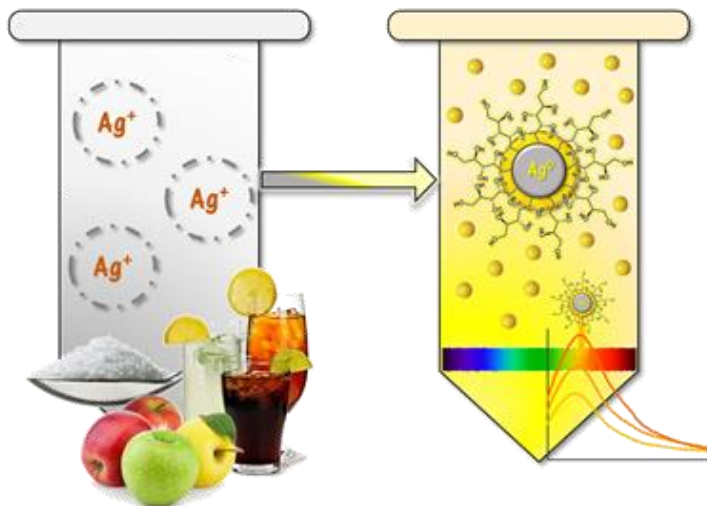
**Work  
in  
progress**

**Future  
perspectives**

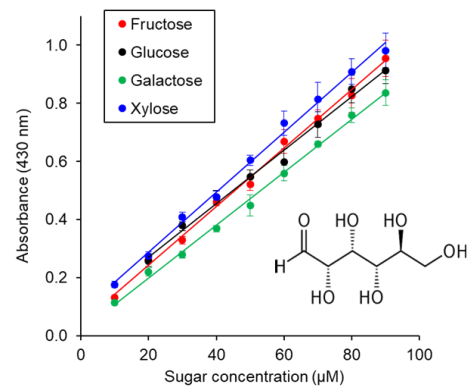


AgNPs  
Sugar

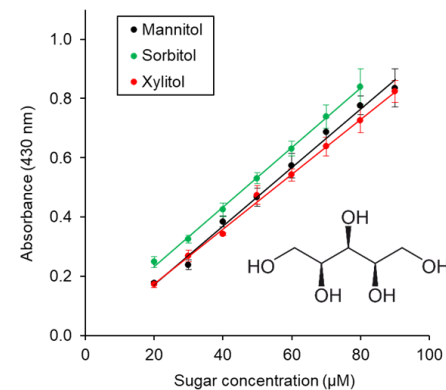
Sugar Content  
Evaluation



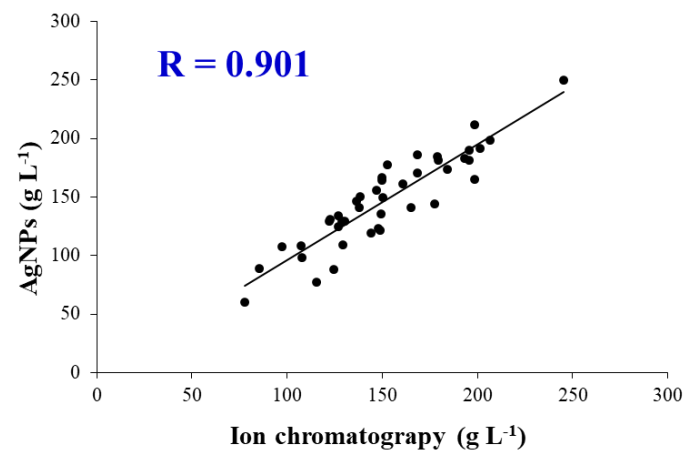
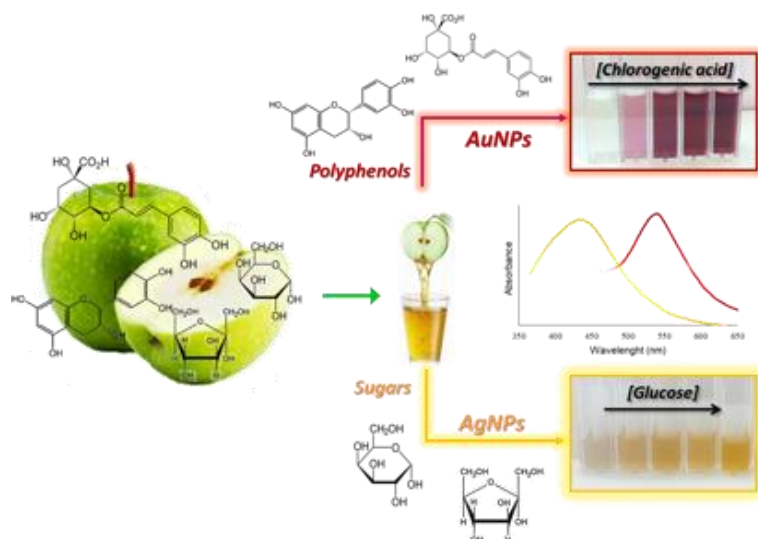
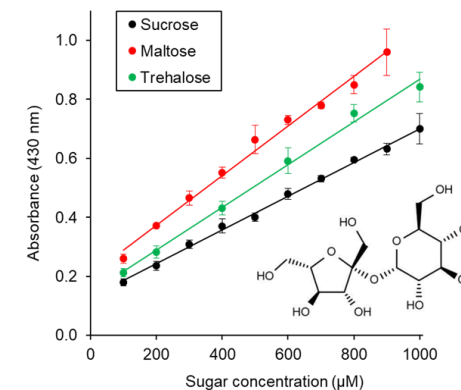
### Monosaccharides



### Polyols



### Disaccharides



Analytica Chimica Acta 1051 (2019) 129–137



Silver nanoparticles-based plasmonic assay for the determination of sugar content in food matrices

Flavio Della Pelle<sup>a</sup>, Annalisa Scroccarello<sup>a</sup>, Simona Scarano<sup>b</sup>, Dario Compagnone<sup>a,\*</sup>

<sup>a</sup> Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023, Teramo, Italy  
<sup>b</sup> Department of Chemistry 'Ugo Schiff', University of Florence, Via Della Lastruccia 3-13, 50019, Sesto Fiorentino, Italy

Food Research International 119 (2019) 359–368



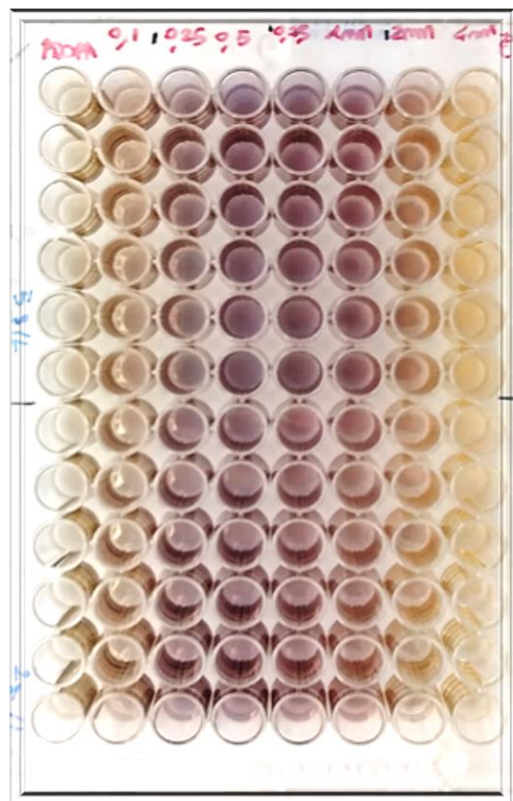
Silver and gold nanoparticles based colorimetric assays for the determination of sugars and polyphenols in apples

Annalisa Scroccarello, Flavio Della Pelle, Lilia Neri, Paola Pittia, Dario Compagnone<sup>\*</sup>

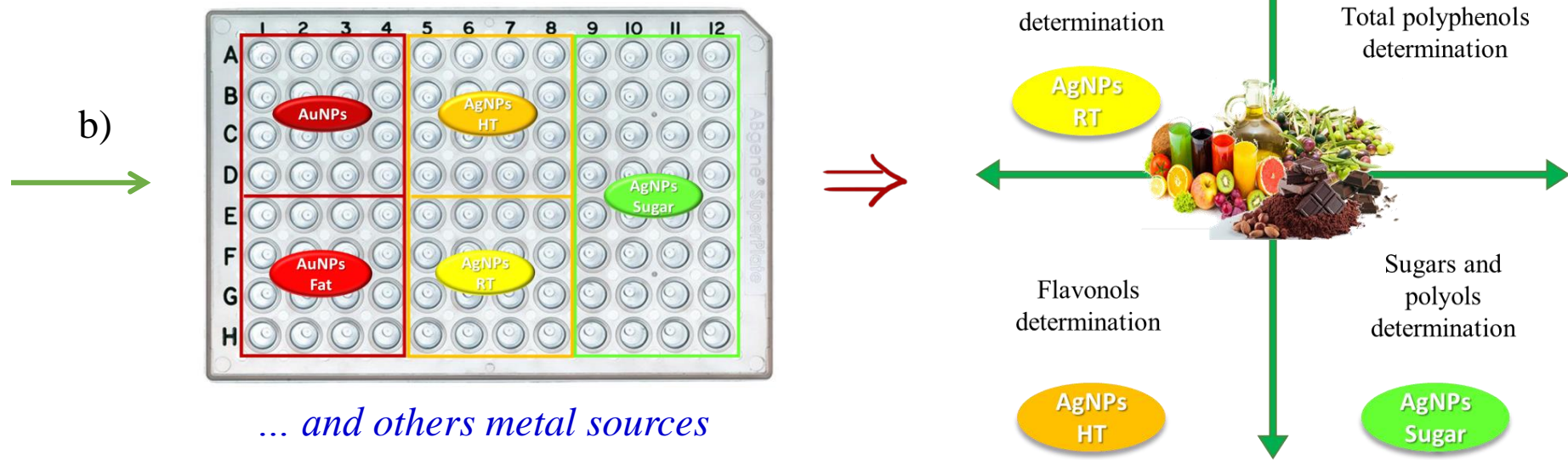
Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023 Teramo, Italy

# MNPs kit and devices realization

**Future perspectives**



## Multi-MNPs kit devices for food fingerprinting



# Aknowledgements:

Flavio Della Pelle, Annalisa Scroccarello, Daniel Rojas (**Rep-Eat H2020-MSCA-COFUND-2015**) Michele Del Carlo, Alberto Escarpa (University of Alcalà)



*Review*

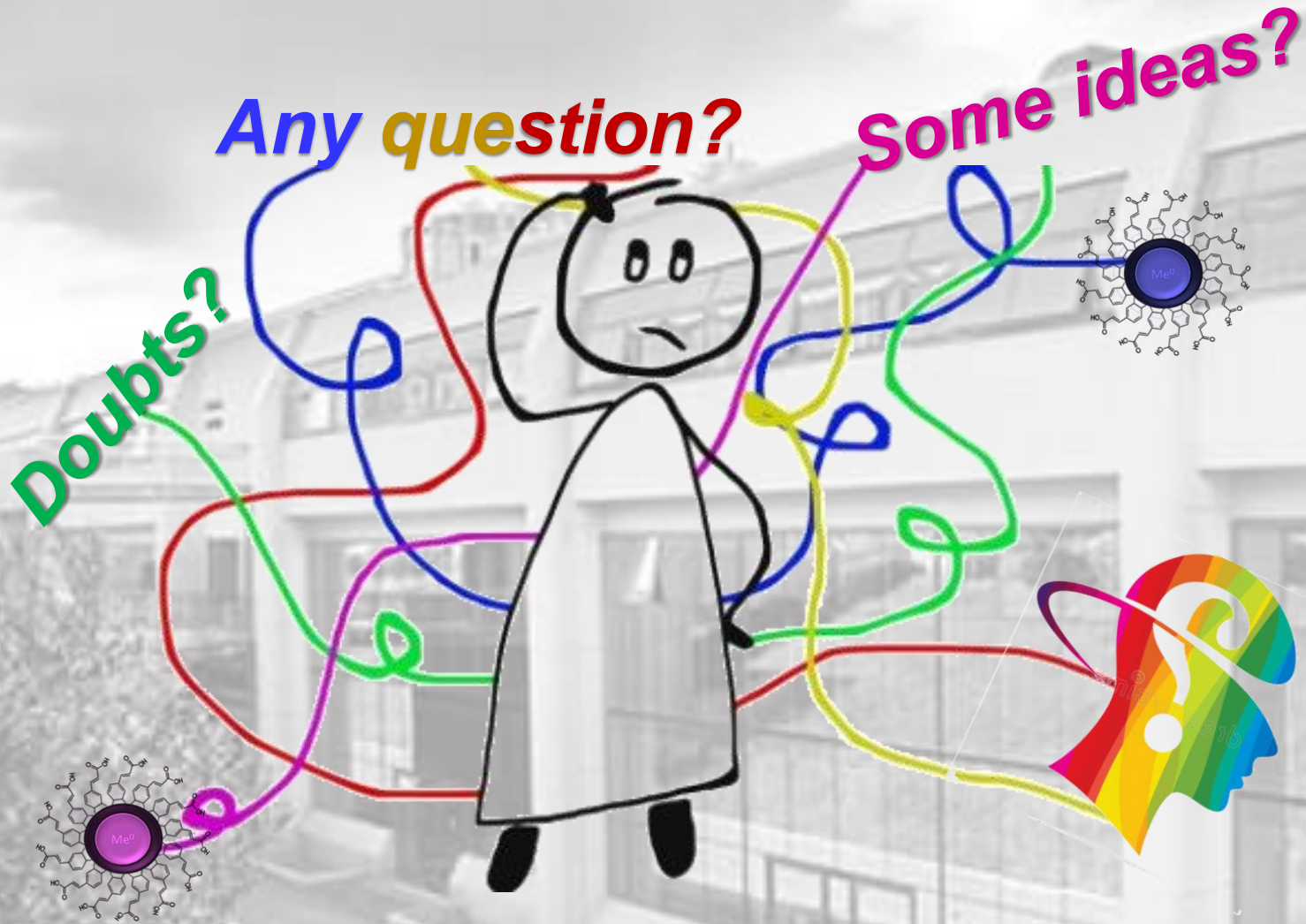
## Nanomaterial-Based Sensing and Biosensing of Phenolic Compounds and Related Antioxidant Capacity in Food

Flavio Della Pelle  and Dario Compagnone \* 

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023 Teramo, Italy; fdellapelle@unite.it

\* Correspondence: dcompagnone@unite.it; Tel.: +36-0861-266942

Received: 20 December 2017; Accepted: 31 January 2018; Published: 4 February 2018



*...Thanks for your attention...*